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William H. Smyrl (principal investigator)

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University of Minnesota
Minneapolis, MN 55455

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WORKSHOP ON DISPOSABLE FUEL CELLS

Edited by

William H. Smyrl
e-mail: smyrl001@maroon.tc.umn.edu
phone: (612) 625-0717
fax: (612) 626-7246

University of Minnesota
Corrosion Research Center
Department of Chemical Engineering and Materials Science
Minneapolis, MN 55455

and

Peter S. Fedkiw
e-mail: fedkiw@aro.ncren.net
phone: (919) 549-4209
fax: (919) 549-4310

Chemical and Biological Sciences Division
U.S. Army Research Office
Research Triangle Park, NC 27709

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VI. List of Attendees

I. EXECUTIVE SUMMARY

Objectives of the Workshop

The objective of the present workshop was to assess the feasibility of a low-power disposable fuel cell. The technological basis for the concept was evaluated along with the barriers that must be overcome for its development. The scope was limited to systems with a useful life of 500 hours or less and a power production of 1 kilowatt or less. Table 1 reveals that such a system would have advantages related to mass over competitive batteries or other power systems, and this workshop compared other characteristics of such systems as well. Disposable devices infer that a major consideration will be the cost, but there is also implied a limited environment burden.

Table 1. Comparison of Energy and Power Requirements (after Owens, 1994).

User Objective	Individual System	
Power	40 to 400 (W)	
Energy	≤ 5000 (Wh	
Mass	2 to 5 (kg)	
Use Time	≤ 72 (h)	
Shelf Life	≤ 10 (y)	
Temperature (ambient)	-40 to 70°C	
Safety	High Priority	
Power Density	50 to 200 (W/kg)	
Energy Density	≤ 2500 (Wh/kg)	
	Mass (kg) For	
	500 Wh	5000 Wh
Battery	10 kg	125 kg
Stirling Engine	70 kg	0.8 kg
Fuel Cell	0.5 kg	0.8 kg

The analysis of research and development needs of disposable fuel cells is based on the following considerations:

*   Efficiency and degradation in performance of fuel cells depends on facile electrode interfacial reactions and coupled transport in the adjacent phases. For polymer electrolyte fuel cells considered here, fuel is supplied in either gaseous or liquid form and the electrolyte is a solid polymer material.

*   The reaction zone is a three-phase region between the electrocatalytic current collector, the fuel phase, and the ionically conducting phase. The distribution of the electrocatalyst on the current collector may be nonuniform which will introduce uncertainties regarding the efficient utilization of the fuel and catalyst.

*   The polymer electrolyte phase must have good ionic conductivity combined with low permeation of the fuel reactants. The solid nature of the electrolyte hampers study of the electrode interfaces, and especially the three-phase region which is largely inaccessible to microscopic monitoring and investigation.

*   Disposable, small fuel cells have an increasing fraction of their total mass and volume that is devoted to packaging, hardware, and electrical connectors as their size is decreased. Thus, scale-down from larger units may result in sacrifices of specific energy and specific power.

Workshop Recommendation for Research

The consensus of the participants was that a disposable fuel cell (DFC) is a viable concept and that there is merit pursuing its development. The cell types and chemistries which were identified as candidates for a DFC include PEM hydrogen/air, PEM methanol/air, metal/air (Al, Zn, or Li), and alkaline-membranes with hydrogen or methanol as a fuel. A number of concerns were identified in the development of a DFC which are common to it and the more conventional cell, e.g., rapid startup, response to transient high-power demand, low-temperature performance, and hydrogen storage method. The state-of-technology is such that modification of present PEM hydrogen/air cells to yield a DFC would be a short-term research undertaking and, at the other

extreme, the Li/air system would be a long-term program. A 500-hour lifetime brings up for reconsideration many materials which were previously discarded for lack of sufficient life. For example, the commonly used perflorinated PEM (i.e., Nafion) might be replaced by a lower cost, hydrocarbon-based membrane; bipolar plates might be constructed of coated aluminum or carbon molded with a binder resin; and thermoplastics such as polypropylene could be used in place of expensive materials such as teflon for gaskets, cell frames, manifolds, etc. Although no new fuels were recommended the oxidation of methanol in a hydroxyl-exchange membrane fuel cell is worthy of study. The methanol oxidation and oxygen reduction kinetics are inherently faster in a basic media which should lower catalyst costs. The carbonate buildup in the basic environment in the membrane, however, might be a significant detriment, and the lifetime of the membrane might not be sufficient. A significant advantage of the 500-hour lifetime is that the testing and evaluation of a device could occur relatively quickly (e.g., within a month) and this would significantly accelerate the test-fix cycle in a development program.

II. INTRODUCTION

The concept of a disposable fuel cell originated at the "Prospector VII: Small Fuel Cells for Portable Power Workshop" held in the fall of 1994 which was cosponsored by the U.S. Army Research Office and the Space Power Institute at Auburn University. The mission times for person-portable fuel cells may typically be measured in tens to hundreds of hours, yet the reviews presented at the Workshop of state-of-art, person-portable fuel cells demonstrated that cell materials (i.e., electrocatalysts, electrolyte, bipolar plates, flowfields, etc.) and chemistries (hydrogen/air or methanol/air) are identical to those under consideration for applications such as transportation in which the lifetime of the system must be in the thousands of hours for commercial viability. While this is legitimate line of inquiry and has been a fruitful pursuit, the question arose if there is merit in pursuing the concept of a disposable fuel cell with a lifetime measured in the hundreds of hours. Specifically, with such a lifetime are there materials and/or chemistries which might be applied to yield a low-cost fuel cell without sacrificing the performance of present state-of-art, long-lived cells? As a means to examine and explore this concept, a group of internationally recognized experts with backgrounds in electrochemical science, materials engineering, and manufacturing of fuel cells and fuel-cell systems was selected for this two-day workshop. The present Proceedings Volume is a record of the speakers' presentations and the recommendations made by the participants

The objectives of the workshop were: (1) assess the viability of the concept of disposable fuel cell; (2) identify trade-offs which define disposable vs. nondisposable; (3) determine if critical paths exist in the requisite science and engineering with an emphasis on: electrode, electrolyte, electrocatalyst, current collector, container, and fuels; and (4) construct a list of research needs to advance the concept to reality, if deemed appropriate. As a working definition, a disposable fuel cell was defined to be a cell with 500 hours maximum (cumulative) lifetime, low cost, and environmentally benign. Cells in the 50-100 W power production range were the focus.

The format was a series of invited presentations on the first day followed by working group discussions on the second. The presentations and follow-up questions and answers set the

stage for break-out group discussions. Two working groups were formed and given specific charges by the Workshop coordinators: one group addressed materials requirements and the other nano- to macroscale systems integration issues. The chairperson of each group prepared a briefing delivered to all participants at the end of the Workshop which summarized the group's deliberations and recommendations. A written summary from each Working Group follows the speaker's summaries in this Proceedings Volume. The charge given by the Workshop coordinators to each working group is given below.

Charge to Working Group on Materials Requirements

For small scale, portable devices, analysis of requirements of energy and power show that fuel cells have a distinct advantage of the mass required to deliver energy in the range of 500 to 5000 watt-hours and power in the range of 50 to 1,000 watts. In order to fully evaluate the concept of disposable fuel cells, it will be necessary to assess the materials requirements for such systems as well. The materials issues to be addressed include those related to: 1) identify the fuels that might be used for disposable fuel cells; 2) identify which fuels require development of new polymer electrolytes; 3) assess the operating temperature and other conditions for the candidate systems; 4) determine if new container materials must be developed, and; 5) construct a research agenda for the electrodes (including electrocatalysts) and current collectors that must be developed for the candidate systems.

Specific questions for focus might be (but are not limited to):

- What are materials requirements for disposable fuel cells? Do the materials now exist? Any specialty (unique) materials?
- What are the limitations caused by materials requirements?
- What research is needed to overcome the limitations? New materials?
- What are the prospects that the research will lead to major advances?

<u>Charge to Working Group on Nano- to Macroscale Systems Integration</u>

Closely coupled with the consideration of materials for a disposable fuel cell (i.e., electrodes, electrolytes, and fuel/oxidizer source) is the concern of how the various component levels (nano-, meso-, and macroscale) might integrate into a small-scale, portable power source. Clearly, there are research and technology issues common to the development of disposable as well as "conventional" portable fuel cells, and both should be considered in the deliberations. However, given a target service life of 500 hours or less at 50-1,000 W power production, the objectives of the Group are to (1) assess the viability of the concept of a disposable fuel cell; (2) identify system trade-offs which define disposable vs nondisposable; (3) determine if critical paths exist in the science and/or engineering necessary to develop a disposable fuel cell, and; (4) construct a research agenda to address these issues.

Specific questions for focus might be (but are not limited to):

- What set of unique requirements (e.g., cost and environmental impact) does the demand of "disposability" define? Do metal/air systems have additional concerns that must be addressed?

- At the nanoscale: What are the requirements for catalyst preparation and dispersion? Could composite polymer electrolyte or gel electrolytes play a role?

- At the mesoscale: Upon consideration of fuel source, would optimal membrane and electrode assemblies (MEA) differ from those in conventional, PEM cells. If carbon dioxide is formed, are there MEA structures that might be advantageous in removing off-gas?

- At the macroscale: Are thermal and water management problems different from conventional PEM cells? Would purity of air supply be more or less of a concern? Can the cells be designed with attitude insensitivity?

III. A. Report of Working Group on Materials Requirements for Disposable Fuel Cells

Chairman: Robert Savinell

The working group developed a list of attributes related to the development of fuel cells for military applications. The list of attributes are given in Table 2. The focus of this workshop is to consider the concept of utilizing fuel cells as a replacement for batteries for extended missions.

Priority	Attribute	PEM	PEM	Bio	Li	Zn	Al	Alk	OHEM
		H_2	DMFC	FC	Air	Air	Air	Fc	
High	Reliable	S	M	L	L	S	L	S	M/L
High	Performance	M/L	M	L	L	S	S	M/L	L
High	Safe	S	S	L	L	S	M	M	S
High	Rapid Start	S	S/M	L	L	S	L	S	S
High	User Friendly	S	S	L	L	S	L	M	S
High	Shelf Life	S	S	L	L	M	S	M	M
H/M	Cost	S	S/M	L	L	M	M	S	M
Medium	Temp Range	L	L	L	L	M/L	M/L	S/M	L
Medium	Humid Range	S	S	L	L	S	S	S	S
Low	Lifetime	S	S	L	L	S	S	S	S
Low	Multiple Start	S	S	L	L	S	S	S	S

Key: S = Short; M = Medium; L = Long

The notion is that the life of the fuel cell may not need to exceed 500 hours. These attributes were prioritized in terms of their importance. A high priority indicates that the attributes must be satisfied while a low priority indicates that for this application the attribute is not as important. Next, the working group considered the various fuel cell systems. Several systems were eliminated from consideration due to obvious conflicts with needed attributes of high priority. The

eliminated fuel cell systems include solid oxide and molten carbonate. The systems considered further were PEM (with fuels of hydrogen, methanol, and other small organic molecules) and biofuels. The metal air systems were included, specifically lithium, zinc, and aluminum. Alkaline hydrogen fuel cells systems also were included, both liquid and polymer electrolyte types.

Each fuel cell and attribute were considered in terms of their need of research and development activity. Table 2 summarizes the discussion by indicating a S, M, or L which corresponds to short term (technology in place), medium (some R&D is necessary), and L (a longer term R&D program will be necessary). In the following paragraphs are brief summaries identifying major critical issues facing the implementation of these technologies.

PEM Hydrogen/Air Fuel Cells: Materials R&D Needs Identified

(1) Performance: The main barrier to competitive performance of hydrogen fueled PEM fuel cells as batter replacements has been limited hydrogen storage capacity in safe form.

To achieve competitive energy densities (in excess of 200 Wh/kg) for missions of ten hours, the most important development required in the field of hydrogen/air PEM fuel cells is hydrogen storage with weight percent hydrogen of about 4%. To satisfy, at the same time, safety requirements, storage in solid state is preferable to gaseous storage at high pressure. Storage in the form of a chemical system for generation of hydrogen (e.g., water + hydrogen releasing solid) is probably an intermediate priority.

Comment: Some relaxation of the storage density requirement could be achieved by an increase of the net power density of the PEM fuel cell stack 100 W/kg in air breathing or forced 1 atm air convection mode.

(2) Temperature range: A weak aspect of the PEM fuel cell is the very limited performance below the water freezing point. This is caused by problems to do with water freezing in various parts of the system, but the most fundamental problem has to do with the drop of protonic conductivity in the membrane electrolyte with temperature. It is suggested that a long-term effort should be considered to try to improve membrane conductivity at a temperature below the water

freezing point. Design of new ionomers with enhanced proton mobility at $T < 0°C$ could be based on (1) fine tuning of properties of PFSA membranes (e.g., lower EW, etc.) taking advantage of the limited life requested in these applications, or more radical changes, such as imbibing in liquid electrolyte (solution for one-time-operation only).

As long as an alternative membrane material for $T < O°C$ has not been provided, effective modes of start up from very low temperature have to be demonstrated. This is not considered a tough problem but should be demonstrated for each startup mode proposed to satisfy "Start Up" requirements.

Comment: Freeze-thaw cycling without resulting loss of PEM stack performance under ordinary operation conditions has been demonstrated for some cell/stack configuration.

Direct Methanol Fuel Cells

Rapid Start Up (Short/Medium): Because of the low power of the DMFC at temperatures of 25°C or below, brining the cell temperature up by cell shorting could be too slow. Solutions are required; for example, temporary operation on hydrogen (from hydride storage) or on hydrogen/methanol mixtures, catalytic methanol/air recombination at the cathode catalyst.

Performance (Medium): Cross-over of methanol through the membrane electrolyte has been identified as the strongest present day deficiency. Membranes of lower methanol flux AND satisfactory protonic conductivity (such as to suffer only minimal, or zero lowering in voltage efficiency) are the highest priority materials research target.

Reliability (Medium): Questions of performance stability are still open, to do with the stability of anode cathode catalysts as well as other electrode and membrane properties under DEMFC operation conditions. The work required to answer these questions includes DMFC testing with effective diagnostics and development of alternative electrode materials and structures to enhance long-term stability and reproducible performance. Another key to achieving the "Reliability" requirements could be a "methanol stopping membrane" of sufficient protonic conductivity which could minimize those problems associated with methanol cross-over.

Cost: Lowering anode catalyst loading while maintaining performance is required to lower cost.

Temperature Range: See discussion of a low T membrane for the PEM fuel cell, as well as Start-Up issues for the DMFC.

Biochemical Fuel Cells

These systems are thought to be in need of long-term research efforts to prove feasibility of the concepts and for development of catalyst and electrode structures.

Lithium Air System

This system is considered to be one in need of long-term commitment for development. A major need is for a membrane electrolyte having good lithium ion conductivity over a temperature range of -40°C to 70°C in the range of at least 10^{-3} S/cm at the low temperature end. In addition, the membrane must have low oxygen and water permeation to protect the lithium electrode.

The system also requires the development of oxygen gas-diffusion electrodes. In particular, these electrodes must be capable of operating in nonaqueous electrolytes with 4-electron transfer (must eliminate peroxide and superoxide intermediates).

In general, low toxicity, and low cost are key factors which must be addressed.

Zinc-Air

In order to achieve long-shelf life, mercury free zinc powders with high stability in alkaline electrolyte must be developed and/or confirmed. For long-shelf life, like ten years, a long-term development effort may be needed.

The low temperature capability to startup may be a limit to this system as it is for the other alkaline system. Certain applications where this system is especially suited for (like soldier air-conditioning system) my make this a nonissue.

Aluminum-Air

The system may not meet the needs for rapid startup since on standby the electrolyte will have to be kept out of the stack. Otherwise, caustic corrosion of aluminum will take place which consumes fuel and generates hydrogen byproduct. Although there are some aluminum alloys which minimize corrosion, the problem persists and could be significant at higher temperatures. Hydrogen generation and accumulation may be considered also as a safety issue for this system. Therefore, anode alloys with low or no caustic corrosion may need further development.

Another major issue is reliability, especially considering the complexity of the system (pumps, filters, blowers, etc.) and the fact that there is virtually no record of operating history. Other issues include ability to operate at low and high temperatures.

Alkaline Hydrogen Fuel Cells

Both liquid electrolytes and anion conduction polymer electrolyte (OH-EM) were considered. The primary issue of hydrogen storage common to the PEM system still persists. Both solid state and safe gas storage development efforts are needed. Although the alkaline systems may operate at lower temperatures better than acid electrolytes, efficient startup performance at low temperatures must still be demonstrated. KOH creepage is viewed as a potential problem to safety and shelf life which will require better material seals. In the case of anion polymer electrolytes, materials for this application are generally not available (low conductivity and unstable).

III. B. REPORT ON WORKING GROUP ON NANO- OR MACROSCALE SYSTEM INTEGRATION ISSUES

Chairman: Jay Stedman

Implications of 500-Hour Maximum Service Life

Typical fuel cell life goals are 4000 hours for transportation and 40,000 hours for stationary power installations. The concept of designing for a 500-hour life in a "disposable" fuel cell is hard for the typical fuel cell researcher or development engineer to grasp, having typically spent his career trying to find and develop materials and cell components that are basically invariant with time, or at the least, having a service life measured in thousands of hours.

Our group consensus was that the practical effect of reducing the service life requirements to under 500 hours is to 1) allow an earlier introduction of many of the advanced (lower cost, lighter weight) cell stack components currently under development for other applications and 2) bring up for reconsideration many materials that were previously discarded for lack of sufficient life.

Consideration Limited to Membrane Electrolyte Fuel Cells

It was the group's consensus to concentrate our discussions on fuel cells of the membrane type, primarily Proton Exchange Membranes (PEM) with some consideration of hydroxide ion exchange membranes. This decision resulted from the desire of the group to specifically tell the sponsor what he might do different in his current portable fuel cell programs in light of a reduced life requirement and the fact that we saw no benefit of program modification to any of the metal-air battery efforts due to the 500-hour maximum life requirement.

Stack Technology Options

Advanced cell separator plates based on molding of graphite or carbon with a binder resin are currently under development by several organizations, and the corrosion with time of the

binding resin is an issue. A 500-hour life requirement can probably be met with the present status of development.

A very low cost and light weight separator plate option is based on formed aluminum plates suitably protected with a corrosion resistant plating. The development problem is to maintain the plate integrity for the required service life.

It should be noted that shelf time, although less severe than operating time, will be a factor that must be considered in any estimate of total required component lifetime. (This comment applies to any and all of the fuel cell components discussed in this write-up.)

The present cost of Nafion proton exchange membranes is an obstacle to the commercialization of PEM fuel cells, especially for the cost driven transportation market. Although less important for the portable power market it still must be considered a limitation. The Daiz proton exchange membrane material, based on hydrocarbon rather than fluorocarbon chemistry, is typical of a class of membranes that offer an order of magnitude cost reduction but have undocumented life characteristics. These membranes also provide improved dimensional stability, easing cell manufacturing, and reduced water and activity improving cell water management.

For long endurance capability, the choice of materials for fabricating cell frames, gaskets, and manifolds is limited to high cost options such as Teflon and other fluorinated plastics. For the mission times under consideration, the group felt that lower cost, readily molded thermoplastics such as polypropylene could be used, lowering both material and fabrication costs.

The consensus of the group was that power system components, such as pumps, blowers, and electronics were not items whose technology is affected by 500-hour life requirement. In some cases design choices may be affected, but in general the need for high reliability components dictates the design technology involved, resulting in an inherent life capability of greater than 500 hours.

An interesting discussion the favorable affects of a short-design life on the requirements for endurance and qualification testing was held. Conventionally, there is a requirement to literally test

for years to obtain life limits of conventional fuel cell designs. Accelerated tests have been conducted; in general, one can accelerate cell degradation by operating at higher stresses, but the correlation with time at normal operating conditions remains suspect. With a 500-hour maximum design life, one can run meaningful tests at real conditions in periods of about one month. This provides for fast turnaround test-fix-test cycles, reducing development time and cost. This factor, if properly exploited, can greatly speed the introduction of a portable fuel cell technology into the DoD inventory.

For hydrogen fueled fuel cells, the hydrogen storage means is a knotty problem with no solution optimum for all situations and applications. The primary options have been extensively discussed in the literature and all have been demonstrated with fuel cell power systems. The discussion here is limited to the effects of the 500-hour life requirement on the design and technology requirements of the various options.

High Pressure Tankage. The design, material choice and weight fraction of high performance overwrapped tankage is a function of the required cycle life and ambient conditions. A 500-hour life consisting of 2-hour missions requires 1000 cycles. Such a tank will be lighter than a tank designed for 10,000 cycles.

Metal Hydride Storage. Breaking up of the hydride particles to fines and subsequent loss of capacity is a problem with metal hydrides. The required number of cycles is an important variable.

Chemical Hydrides. These are "one-shot" hydrogen supply elements. There are many technology and design problems associated with development of a safe, high hydrogen yield, hydride subsystem but none particularly affected by a 500-hour life requirement.

Liquid Fuel Processor and Hydrogen Purification. Although not normally thought of as candidates for portable power supplies, recent developments in micro-channel heat-transfer devices give hope that such devices give hope that such devices can be developed for power levels as low as 50 watts, and certainly for the 500-watt requirement of the battery charger mission. As all

catalytic processes are subject to time related performance degradation, a 500-hour life will ease the catalyst and result in lighter components.

Special Factors for Direct Methanol Fuel Cells (DMFC)

The discussion above applies to DMFC, as well as hydrogen fueled cells, (except for the section on hydrogen storage, of course). Several areas of cell component technology are unique to the DMFC and are discussed below.

Cathode catalysts that are unaffected by crossover methanol are under development by CWRU (Macrocycles) and Lynntech (Chevrels). The Macrocycles are known to have limited life, the endurance capacity of the Chevrels are unknown at this time. A life requirement of under 500 hours will allow early evaluation of these catalysts in portable power systems based on direct methanol cells.

The hydrocarbon membrane mentioned above, as well as a membrane based on cross linked polystyrene sulfonic acid and polyvinylidene fluoride, both offer the potentials to greatly reduce methanol crossover in a DMFC fuel cell without significantly reducing cell voltage. Long endurance is questionable for both of these membranes, a 500-hour life will ease the development requirements.

Many real applications for DMFC involve long periods of time at low power output with intermittent bursts of several minutes at much higher power. As we do not expect to completely eliminate crossover, it is expected that the methanol concentration will be lowered during low power operation to improve overall efficiency, requiring some finite time to raise the concentration for optimum performance at the high power point. As the user will undoubtedly require "instant-on" of the high power a hybrid system with a small rechargeable battery is envisioned for most applications. The battery can also provide heat-up energy and user power during start from cold temperatures.

Alkaline Electrolytes

A short discussion was held on the benefits and problems of alkaline electrolytes for hydrogen and direct methanol fueled fuel cells. A first conclusions was that only membrane cells were of interest, as the electrolyte management problems associated with free or capillary matrix cells were judged to be too much to cope with in small portable power applications. There is no accepted off-the-shelf anion (OH-) membrane with long-demonstrated life. However, a 500-hour life may be possible with available membranes.

Other conclusions were that there would be overall performance improvement over PEM cells, but that catalyst costs, especially for direct methanol cells would be lower due to the higher activity for methanol oxidation. A serious question was unanswered on the amount, location, and performance affects of carbonate formed at the anode from the CO_2 product and at the cathode from CO_2 contained in the reaction air. It was mentioned that Argonne National Lab has a contract DARPA to investigate this approach to a DMFC.

Research Priority

At the end of the discussion period we were asked to prioritize areas of fruitful research for a short duration "disposable" fuel cell. The following is the group's recommendations:

1. Expand hydrocarbon membrane R&D

2. Expand aluminum separator plate R&D

3. Support macrocycle and Chevrel cathode catalyst R&D

4. Combine 1, 2, and 3 into cell stacks and conduct endurance tests

5. Support low power fuel processor and hydrogen clean-up development

IV. WORKSHOP ON DISPOSABLE FUEL CELLS

AGENDA

April 11 - *Formal Presentations*

8 a.m.   Welcome by Dr. Peter Fedkiw
         U.S. Army Research Office

8:15   Introductory Remarks by Dr. Richard Paur, U.S. Army Research Office
         Non-fuel Cell Power Sources, Army Needs

8:30   Mr. Jay Stedman, Institute for Defense Analysis
         Overview of ARPA Fuel Cell Program

8:45   Dr. Sol Gilman, U.S. Army Research Lab-EPSD
         Army Fuel Cell Research and Battery Research

9:15   Dr. Harold Christopher, U.S. Army CECOM
         U.S. Army Battery Arsenal

9:45   Dr. Shimshon Gottesfeld, Los Alamos Natl. Lab
         Overview of DOE Fuel Cell Program

10:15   Break

10:30   Dr. Patrick Grimes, Pat Grimes Associates
         Historical Perspectives on Fuel Cells

11:00   Dr. Anthony LaConti, Giner, Inc.
         Disposable Fuel Cells and Lifetimes

11:30   Dr. Oliver Murphy, Lynntech, Inc.
         Innovative Approaches for Fuel Cells

12:00   Lunch in Meeting Room

1:30   Dr. Donald Maricle, International Fuel Cells
         Person-portable Fuel Cells

2:00   Dr. William H. Smyrl, University of Minnesota
         Barriers and Opportunities in Disposable Fuel Cells

2:30   Dr. Günther Sherrer, Paul Sherrer Institute
         Polymer Electrolyte Membrane Fuel Cells

3:00   Dr. Robert Savinell, Case Western Reserve University
         Polymer Electrolyte Membrane Fuel Cells

3:30   Break

3:45   Dr. Charles Martin, Clemson University
         Polymer Electrolyte Membrane Fuel Cells

4:15   Dr. K.M. Abraham, EIC Laboratories
        Lithium-Air Systems

4:45   Mr. Ronald Putt
        Zinc-Air Systems

7:00   Dinner - Radisson Metrodome Hotel

April 12 - *Working Groups*

8:30 a.m.   Discussions
            A - Materials Requirements
            B - Systems Integration

12:00   Lunch in Meeting Room

1:30   Discussions and Report Preparation

3:30   Presentation by each group of findings-summary of recommendations. Wrap-up.

4:30   Workshop Concludes

IV. PERSPECTIVES ON FUEL CELLS

BY WORKSHOP PARTICIPANTS

INTRODUCTORY REMARKS.
NON-FUEL CELL POWER SOURCES, ARMY NEEDS

Dr. Richard Paur
US Army Res Office
AMXRO-CB PO Box 12211
Research Triangle Park, NC 27709

The Army needs better lightweight power sources because soldiers are being issued more and more equipment which requires electrical power. Improvements in reducing the power consumption of a given device, say a laptop computer, are more than offset by the addition of more devices such as global positioning systems.

"Better" can be described in terms of several attributes; higher energy density, higher power density, lower cost, safer, and more environmentally benign quickly come to mind. In order to be affordable for the military, power sources should be useful to a large cross-section of the civilian market. Perhaps the Army will not use exactly the same devices as the civilian market, but the basic manufacturing processes must be similar enough to preclude the necessity for specialized manufacturing lines for the military items.

The Army Research Office has research programs looking at a number of possible power sources which might be better than existing power sources under at least a limited range of conditions. The technologies under study include hydrogen/air fuel cells, direct oxidation of methanol fuel cells, thermophotovoltaic power systems, and micro gas turbine generators. Hydrogen air fuel cells are the most mature technology of the above suite; one serious drawback to their use in the battlefield is the need for a hydrogen distribution system which can provide the soldiers with the necessary fuel. The hydrogen supply problem is being addressed by several Army funded projects as well as work supported by US intelligence agencies, private industry, the Department of Energy and others.

The purpose of this workshop is to consider fuel cell power sources with the goal of determining whether the Army could develop significantly less expensive fuel cells if the units were designed with a modest lifetime goal, on the order of 500 hours, rather than the many thousands of hours that is the typical goal of fuel cell developers. [Many current fuel cell developers have been strongly influenced by the lifetime goals of the power utility industry; most estimates of the lifetime needs for Army applications range from tens of hours to several hundred hours.] In numerous discussions of fuel cell technology, research personnel allude to materials which have been tried in the past, but which have been rejected by the community 'because they don't last'. Further inquiry reveals that in many cases (e.g., some hydrocarbon membrane electrolytes) the lifetime may be on the order of a thousand hours, well in excess of anticipated Army requirements. Considering that in some cases these previously rejected materials are more than an order of magnitude less expensive than their long lived counterparts, it appears likely that fuel cells constructed recognizing that the required lifetime is only about 500 hours could be made significantly less expensively than some of the systems that are produced today.

GEN II Soldier System
Anticipated Power And Energy Requirements
(12 hr mission)
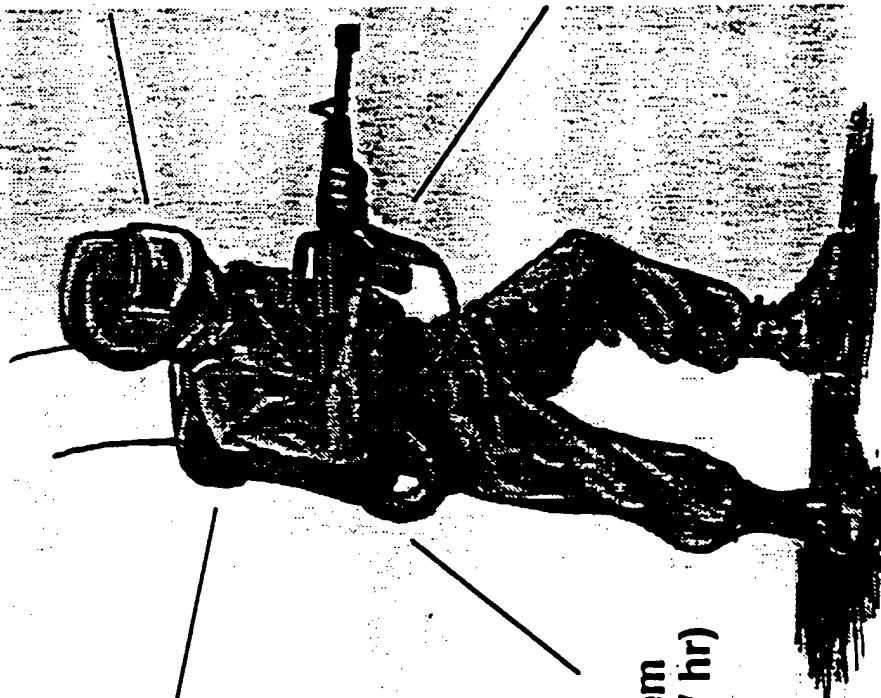
Integrated Headgear Subsystem
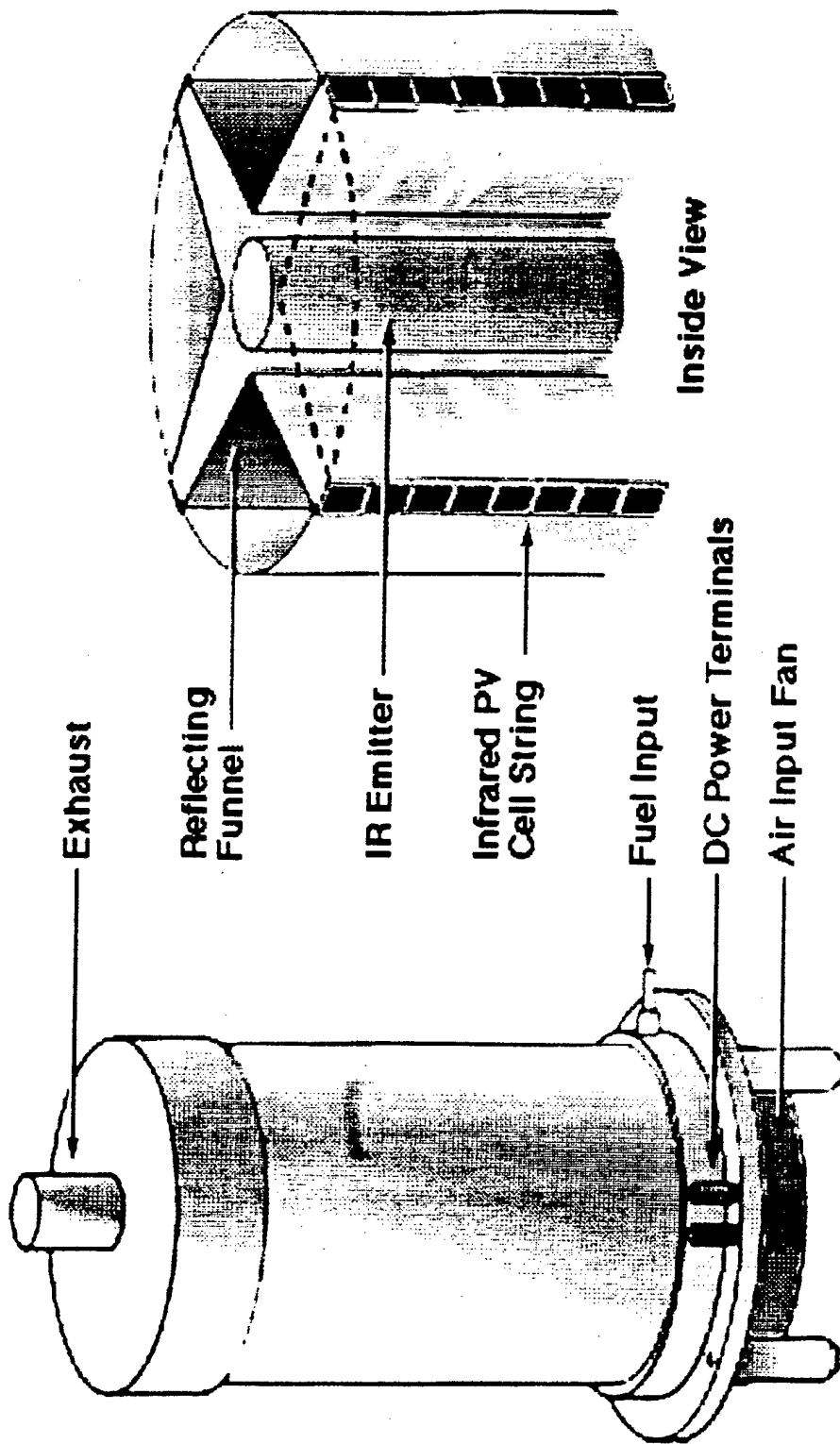(6 W max, 60 W hr)

Weapon Interface Subsystem
(1 W max, 5 W hr)

Individual Soldier Computer/Radio
(30 W max, 120 W hr)

Refrigerated Micro-Climate Cooling System
(150 W max, 4 hr, 600 W hr)

"Battery technology is one of the most important areas that we have right now." Army Gen. Leon Salomon, Commander, Army Materiel Command, 11/23/94

ARPA

Thermophotovoltaic (TPV) Generator

Exhaust

Reflecting Funnel

IR Emitter

Infrared PV Cell String

Fuel Input

DC Power Terminals

Air Input Fan

Inside View

MULTI-FUELED, MULTI-KILOWATT THERMOPHOTOVOLTAIC GENERATOR

OBJECTIVES

Design and Develop a 3-5 kW Thermophotovoltaic Generator with:

- Multifuel capacity
- Low Noise (70 db)
- 26% Overall efficiency with regenerator
- Lightweight (250 w/Kg)
- Clean

APPROACH

- Increase GaSb technology from 3 watts/cm^2
- Develop short pass IR filters
- Extend IR response from 1.7 microns to 2 microns for quaternary cells
- Cast ceramic burner and emitter parts for uniform operation at 1700° C
- Grow GaSb crystals
- Reduce the weight of many parts of burner

ACCOMPLISHMENTS

- Cell inventory includes: 700 standard cells, 80 oversize
- Filter inventory includes 400 filters
- Liquid phase epitaxy equipment is installed
- Crystal puller is being shipped from China
- Lighter weight parts have been designed for burner
- Furnaces are complete and ready to fire ceramic parts
- Instrumentation package as been designed and built
- Emission testing equipment has been purchased
- Ceramic parts have been designed and cast
- CNC mill has been purchased
- Silicon graphics work station and software have been purchased.
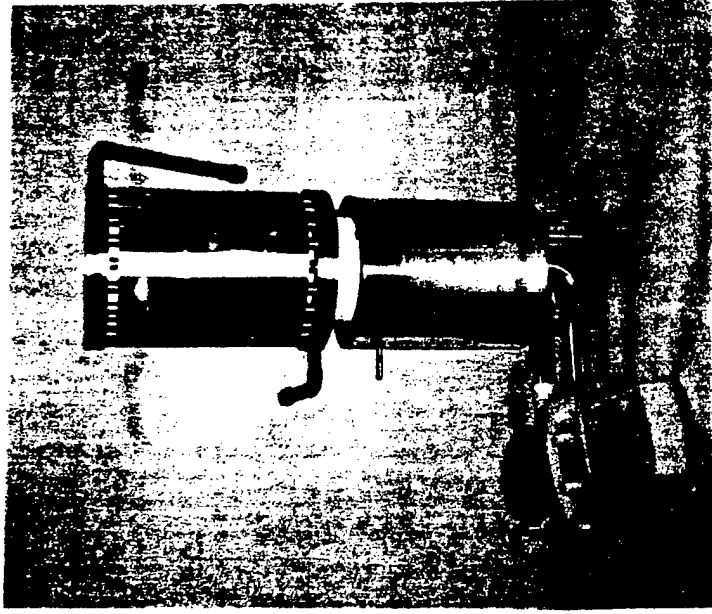
Current 1 kWatt Single Cylinder TPV Burner

VEHICLE RESEARCH INSTITUTE
WESTERN WASHINGTON UNIVERSITY

MICRO GAS TURBINE GENERATORS
- Concept -

- μ Fabrication of refractory ceramics enables the concept of micro gas turbine engines and generators (milli-centimeter dia)

- Power densities can approach those of full-sized engines (100 watts/cc)

- Achieving high performance levels requires
  - High turbine inlet temperatures (~1600°K)
  - High speed, highly stressed rotating parts (3×10^6 rpm)
  - Low leakage and high tolerances (~1 μm)

- Cost could be very low given sufficient demand (10^8 units/year)

- μ Engines can be an enabling technology for new concepts
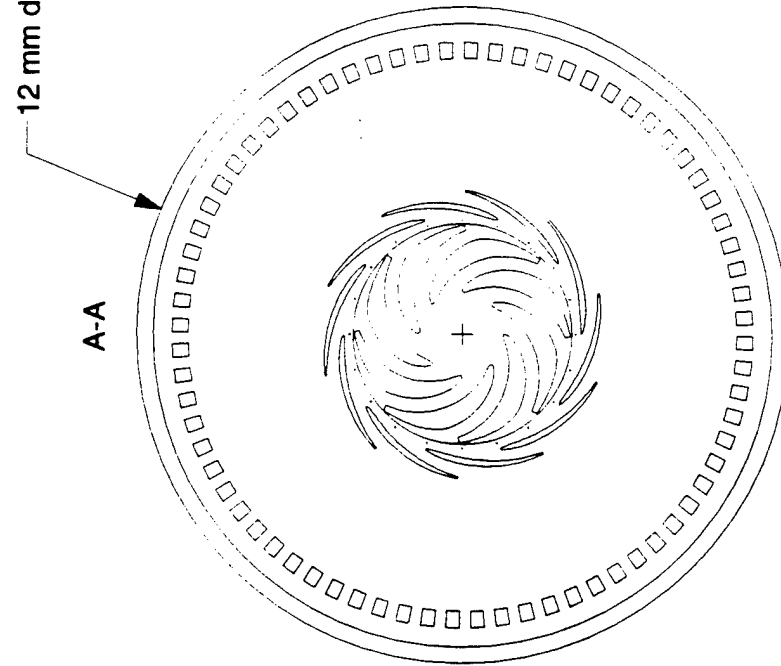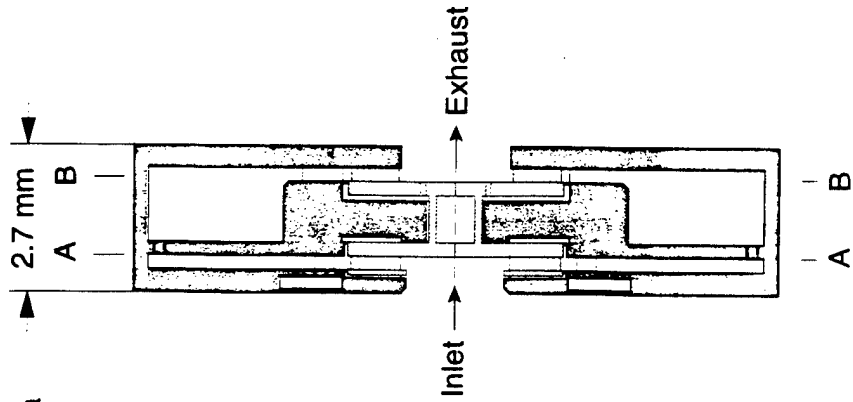
CONCEPTUAL LAYOUT OF μJET ENGINE
(Inlet Flow Area = 1 mm²)

Turbine

B-B

EXHAUST

Bearings

INLET

4 mm

6.4 mm dia

Compressor

A-A
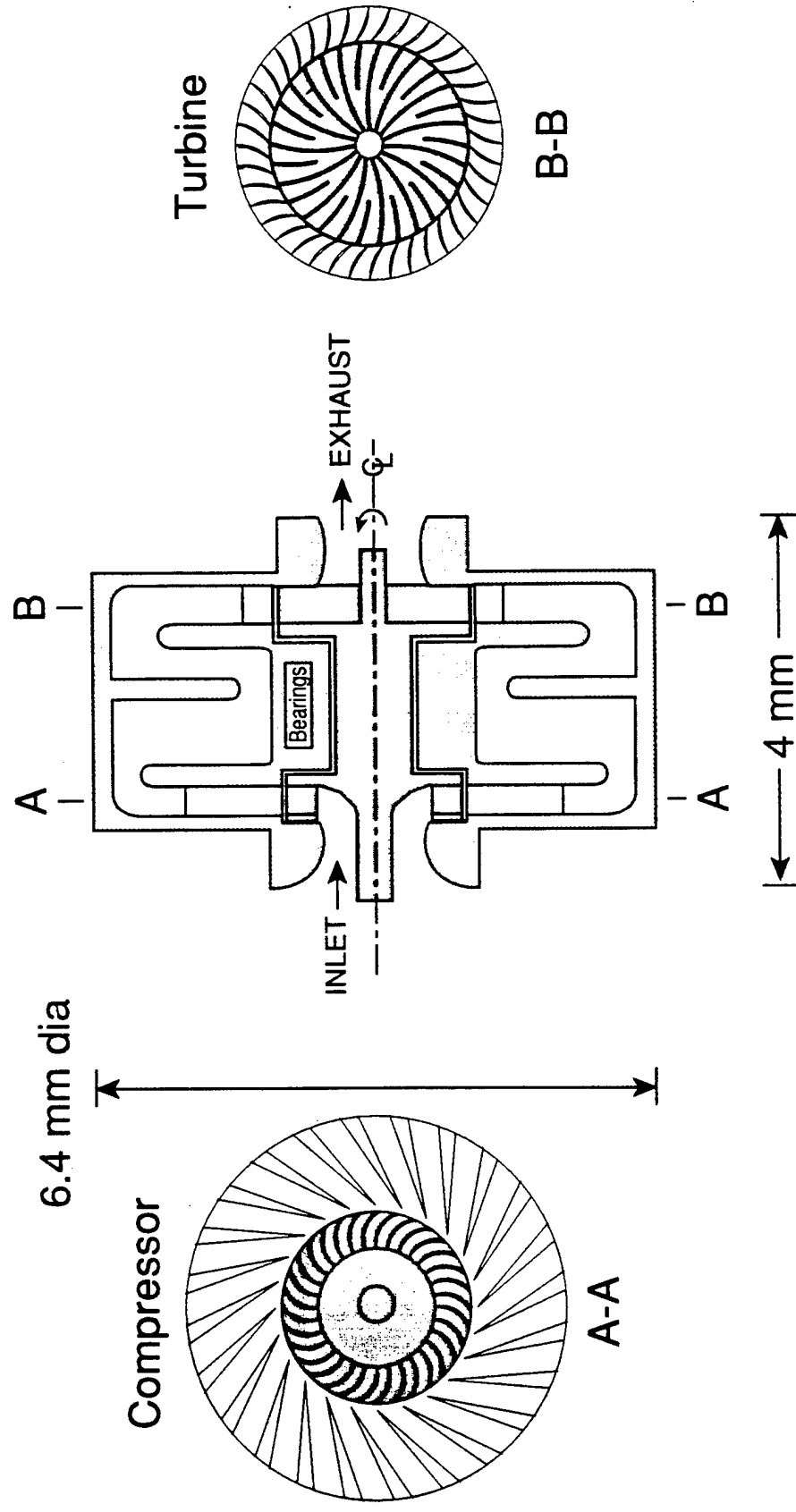
PERFORMANCE COMPARISON

	μ Turbogen + Fuel	LiSO$_2$ Battery (BA5590)
Power Output	50 w	50 w
Energy	175 w-hr	175 w-hr
Weight	50 grams	1000 grams
Size	50 cc	880 cc
Specific Energy	3500 whr/kg	175 whr/kg
Energy Density	3500 kwhr/m^3	200 kwhr/m^3

MICRO GAS TURBINE GENERATOR

Turbine

Compressor

23.57"³

5.00

2.45

Ø2.45

2.00

.60

.80

2.00

FUEL
CELL
#1

FUEL
CELL
#1

ELECTRONIC
CONTROLLER

.45

2.25

.10

3.00

PUMP
#2

PUMP
#1

4.45

CONFIGURATION #4

H POWER CORPORATION
SACRAMENTO, CA.

ENVELEPE

BA5590

DRAWING NO.	BA55R02A	
SIZE		REV
A		A
SCALE:	NTS	SHEET 1 OF 1

OFFICE: CA.
DRAWN BY: AW 11/17/95
CHECKED BY:
APPROVED BY
ISSUE DATE:
CONTRACT NO

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THE EXPRESS CONDITION THAT THE CONTENTS NOT BE USED FOR
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THE ARPA PROGRAM IN ADVANCED FUEL CELL TECHNOLOGY

Lawrence H. Dubois, Director, Defense Sciences Office
Advanced Research Projects Agency
Arlington, VA
March 1996

Today's power sources for military platforms are severely hampered by high cost and a lack of energy/power density. This is particularly true for small (<100 W) power systems, which at present are limited to primary electrochemical batteries. Mission effectiveness may also be hindered by the poor reliability, high exhaust emissions, and excessive noise generation of current diesel generators (3 - 100 kW). For these reasons, the Advanced Research Projects Agency (ARPA) is pursuing a multi-path, multi-disciplinary approach to developing advanced fuel cell technology for a number of critical Department of Defense (DoD) applications. A summary of this program is shown in Figure 1.
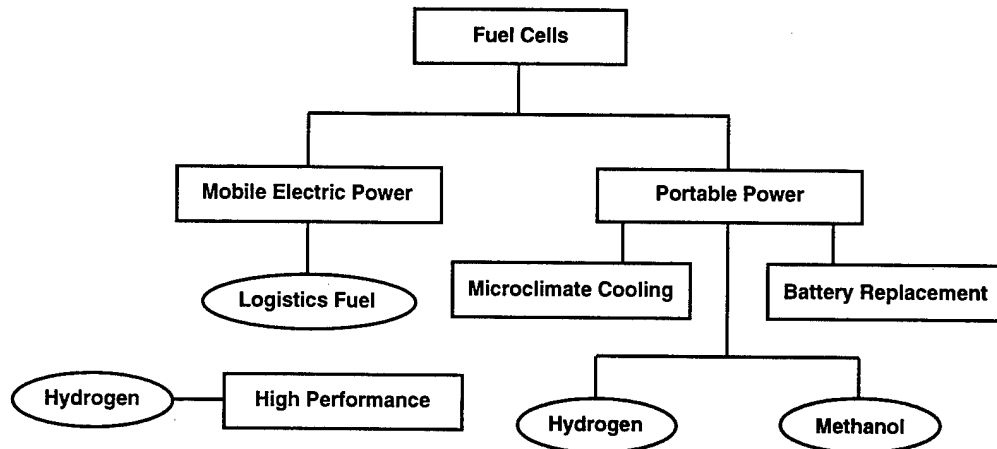

Figure 1: Summary of ARPA Program in Advanced Fuel Cell Technology including the potential fuel for each application.

The current ARPA funded effort in fuel cells has two main thrusts: (1) the replacement of mobile electric power generators, auxiliary power units (for tanks in silent watch and surveillance), and field power stations (for $C^{3}I$ and communications systems) with 3 - 100 kW fuel cells operating on logistics fuel (e.g., diesel or jet fuel) and (2) the development of small (tens to hundreds of watts) power systems for individual soldiers. Potential fuels for these latter systems include hydrogen and methanol. Specific applications involve the replacement of military standard batteries for portable electronics and for microclimate cooling. Larger fuel cell systems may also be used to augment the current power sources used at permanent DoD facilities.

Mobile Electric Power

The Department of Defense, through the Program Manager, Mobile Electric Power, procures, maintains, and upgrades a family of mobile field generators and auxiliary power units by the various Services. These diesel fueled generators range in power output from three to several hundred kilowatts. The present generators could be improved in several key areas of performance and operational characteristics. Thus, in spite of a recent upgrade, they still produce excessive

noise and pollution, are relatively low in efficiency (especially at part power, their normal operating point), require frequent maintenance from skilled personnel, and are considered to be unreliable for critical stand-by power applications.

Fuel cell technology, as being developed for commercial stationary power and transportation applications by industry and the U.S. Department of Energy, has the potential to alleviate many of these problems, however, commercial efforts are focused on the use of natural gas and methanol rather than the heavy hydrocarbon liquid fuels (e.g., diesel and jet fuels) required by the military Services. ARPA has initiated a major research and demonstration program to develop the technology for complete multi-kilowatt fuel cell systems capable of operating on logistics fuels (e.g., DF-2, JP-8). Processing of these heavy liquids to a fuel gas suitable for oxidation in today's fuel cells in general requires higher temperatures than methane or methanol reforming and removal of impurities such as sulfur. Thermal integration is also critical to minimize the part count and to ensure a small package size. The program goals are to develop technologies that will allow logistics fueled fuel cell power plants to be fielded that are competitive with present diesel generators in weight and volume and demonstrate the inherent fuel cell characteristics of low maintenance and high reliability with low noise, negligible emissions, and high efficiency over a wide power range. A summary of the ARPA program is shown in Figure 2.
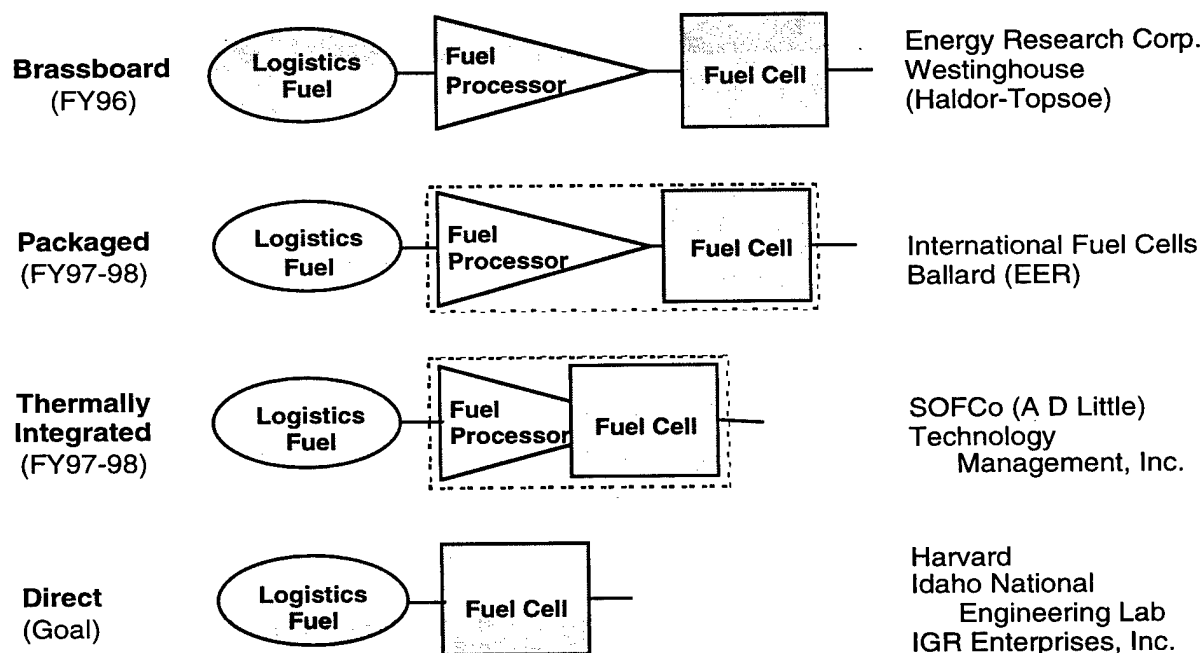

Figure 2. Summary of ARPA mobile electric power program. The expected demonstration dates are indicated on the left. The contractor names (right) shown in parentheses are for the developers of the fuel processor units.

The ARPA program includes: 1) successful brass board demonstrations (~2000 h of operation) of conventional 27-32 kW molten carbonate and solid oxide fuel cell power plants with

an add-on fuel processor (hydrode sulfurizer and steam reformer) for converting logistics fuel to a sulfur-free fuel gas: 2) development of 10 kW solid oxide fuel cell power plants with either a thermally integrated steam reforming type logistics fuel processor or a catalytic partial oxidizer type fuel processor; and 3) a packaged 100 kW phosphoric acid electrolyte power plant with an autothermal logistics fuel processor (Figure 3). An additional collaborative effort between ARPA and the DOT to build methanol-fueled, 100 kW fuel cell power plants (both PEM and PAFC) for transportation applications is also underway.
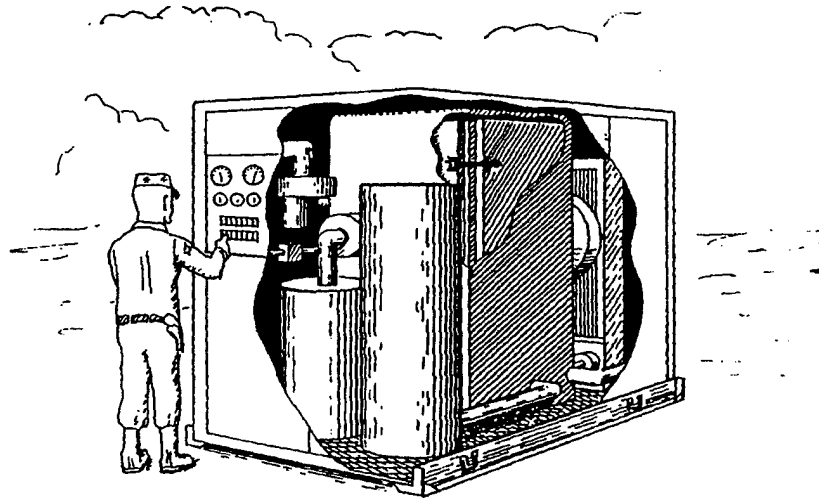

Figure 3. Schematic diagram of a 100 kW mobile electric power plant to be built by International Fuel Cells. The system is based on a phosphoric acid fuel cell with an autothermal reformer.

Finally, several ARPA-funded research efforts are developing new logistics fuel processing concepts (e.g., catalytic cracking (Aspen Systems, Inc.), "unmixed combustion" (Energy and Environment Research), and micro partial efficiencies, small sizes and weights, and a high tolerance to impurities. The possibility of *directly* oxidizing *hydrocarbon* fuels in solid oxide (current performance: 0.6 V @ 60 mA/cm^2 with octane) and proton exchange membrane fuel cells is also being explored. The advantages of this approach are shown in Figure 4. The development and demonstration of direct oxidation fuel cells is the ultimate goal of the ARPA program.

Although the scope of the current ARPA mobile electric power fuel cell program is quite comprehensive, new ideas for converting logistic fuels to hydrogen and carbon monoxide, at high efficiency and with low hardware volume; for the removal of sulfur (and other impurities) from the fuel or fuel gas; and for internally reforming or direct oxidation of logistics fuels in fuel cells will always be considered. It should be noted that despite the success of these efforts, early introduction of fuel cell powered systems into the field may be procluded by both cost and complexity (Figure 4).

Portable Power

The Department of Defense currently spends in excess of $100M per year on batteries (not including maintenance and disposal costs). The largest single application is for the Army where they purchase approximately 350,000 large primary (i.e., use once and dispose) lithium batteries (BA-5590, see below) costing more than $20M per year to power communication, control, and other portable field equipment. A small, simple fuel cell, based on the direct oxidation of methanol (e.g., $CH_3OH + 3/2O_2 \rightarrow CO_2 + H_2O$) in a proton exchange membrane fuel cell, has the potential to replace lithium battery technology in many DoD applications. Methanol is chosen as a potential fuel due to its high energy density (5.6 Wh/g), safely, low cost, ease of handling and distribution,
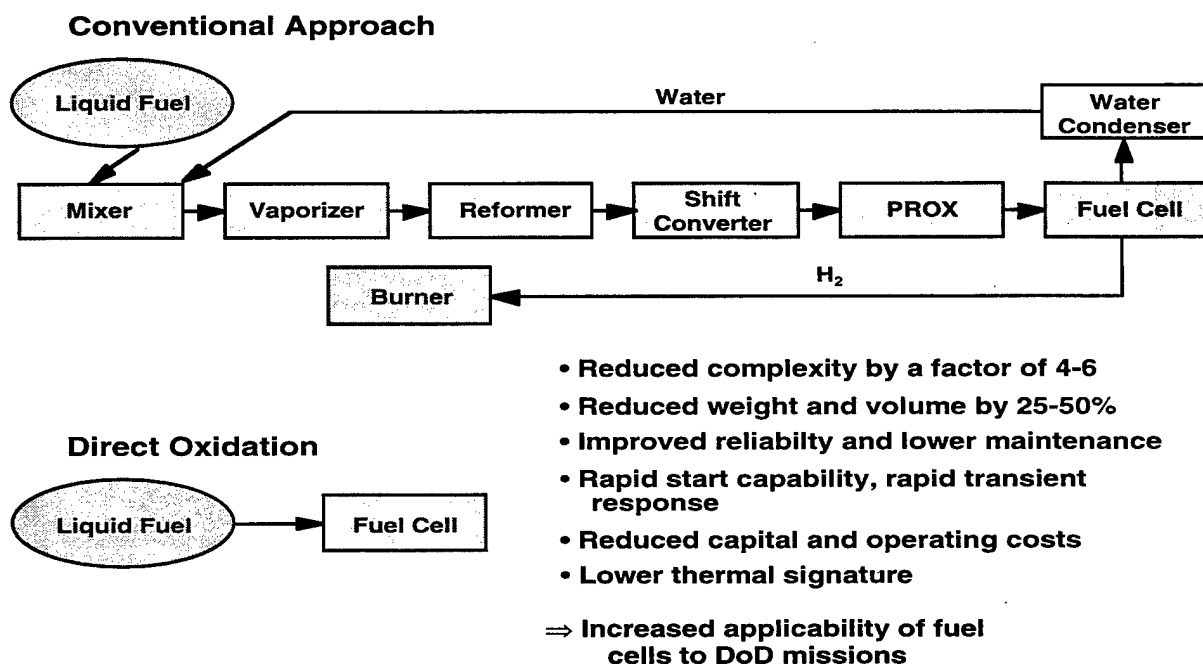
Conventional Approach

Direct Oxidation

- Reduced complexity by a factor of 4-6
- Reduced weight and volume by 25-50%
- Improved reliabilty and lower maintenance
- Rapid start capability, rapid transient response
- Reduced capital and operating costs
- Lower thermal signature

⇒ Increased applicability of fuel cells to DoD missions

Figure 4. The advantages of direct oxidation of liquid fuels vs. the more conventional approach.

and high electrochemical activity (6e-/molecule). The advantages of the direct oxidation approach are summarized in Figure 4. In addition, the use of a liquid feed eliminate the need for cooling plates and fans, thus minimizing the stack size and further simplifying and reducing the balance-of-plant.

The energy density of an *individual* direct methanol fuel cell (DMFC) is estimated to be up to *five times* that of a primary lithium battery. This greatly reduces the weight that a soldier must carry into the field or, alternatively, increases his capability for the same weight. In addition, these fuel cell are not thrown away after each use, but can be "recharged" by simply adding a small amount of additional methanol to the fuel tank. Thus, for extended missions, the "effective" energy density of a direct methanol fuel cell can be tens or even hundreds of times that of a primary battery. These features offer a great incentive for ARPA to sponsor electrochemical and materials research activities aimed at developing the basic technology and in demonstrating the operational characteristics in prototype hardware.

Recent advances in the performance of individual direct methanol oxidation fuel cells have yielded power outputs of nearly 350 mW/cm^2 (0.5 V at 680 mA/cm^2) and four-cell stacks approaching 180 W. The operating efficiency is between 30 and 35% (at <300 mA/cm^2) and the fuel utilization is near 85%. Individual cells have run for more than 200 hours (>200 h continuous) and 50 W stacks have operated for over 1600 h (more than 25 start/stop cycles) with no significant poisoning. These cells and stacks will self-start from ambient temperature (20°C) and can be run on atmospheric pressure air (up to 0.3 V at 450 mA/cm^2). Thus, the present state-of-the-art is close to being sufficient to build a DMFC that will match the output of the most widely used high capacity DoD lithium battery (the BA-5590) at the same weight and volume (a breadboard unit is currently under construction, see Figure 5). As a first step in this endeavor, H Power Corporation is building a hydrogen fueled-PEM version of this system. A metal hydride was chosen as the initial fuel storage medium due to its simplicity and moderate energy density
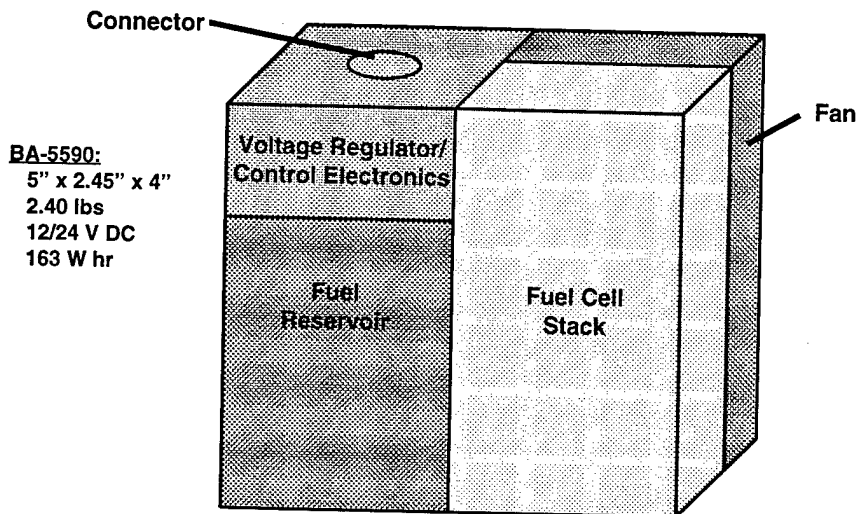
Connector

Fan

BA-5590:
5" x 2.45" x 4"
2.40 lbs
12/24 V DC
163 W hr

Voltage Regulator/
Control Electronics

Fuel
Reservoir

Fuel Cell
Stack

Figure 5: Schematic diagram of a fuel cell equivalent of a BA-5590 LiSO$_2$ battery.

($\sim$1.8 wt % H$_2$). Much will be learned about component sizing, water and thermal management, and system integration from these early experiments.

In it's four years of existence, ARPA's Advanced Fuel Cell Technology program has increased the power density of a direct methanol oxidation fuel cell by more than a factor of ten over the best previous results (e.g., from less than 30 to nearly 350 mW/cm^2). This performance enhancement could only be possible through a strong, focused approach involving close interactions and frequent discussions between universities, federal laboratories, small businesses, and industry (Figure 6).

Considerable work remains to be done, however, if the full potential of the direct oxidation fuel cell concept is to be realized. For example, in order to improve the fuel utilization and to raise the overall system efficiency, both an improved anode catalyst and a high ionic conductivity membrane with reduced fuel crossover must be developed. Current efforts are therefore aimed at: 1) increasing the catalytic activity of the Pt-Ru anode for the oxidation of methanol by the optimization of catalyst structures and by the addition of a third metallic constituent and/or an organometallic complex, 2) reducing the cross-diffusional loss of methanol from anode to cathode by modifying the proton exchange membrane or by synthesizing on alternative membrane material with a lower inherent crossover (a consequence of this will be the ability to operate on a higher concentration of methanol and, therefore, to improve performance further), 3) developing a substitute for the present platinum cathode catalyst that will be unaffected by methanol, 4) enhancing electrochemical performance through the use of alternative high energy density liquid fuels, 5) testing liquid and/or solid oxidants to allow air-independent operation, and 6) developing low-cost, light weight materials and novel assembly concepts for separators, flow fields, and end plates.

Based on the success of the program to date and on the developments expected within the next 6 - 12 months to improve cell and stack performance and efficiency, it is anticipated that ARPA will initiate the procurement of one or more prototype demonstration units designed to meet this and other specific DoD requirements.
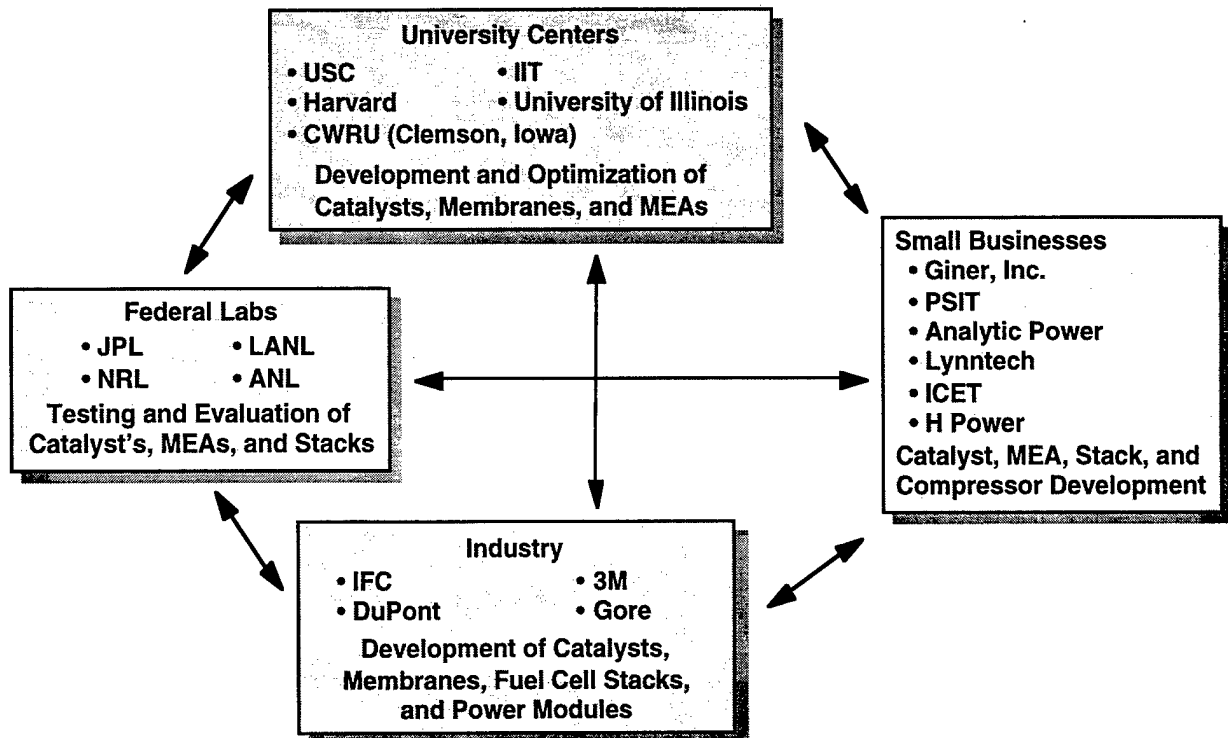
Figure 6. Team approach to the development of direct methanol oxidation fuel cells. The double-headed arrows indicate significant interactions between these different groups.

High Performance Fuel Cell Initiative

Underlying the two main thrusts outlined above is the realization that fuel cells will only be used if 1) their performance (e.g., mass and volume energy densities) is high and 2) their costs are low. In order to stimulate the development of such systems, ARPA is sponsoring three fuel cell development programs in its High Performance Fuel Cell Initiative. These included the development of proton exchange membrane and solid oxide fuel cell systems operating on hydrogen and air at 1 *atmosphere of pressure and greater* than 1 kW/kg and 1 kW/l. Current single cell performance is now adequate to reach these goals (PEM: 0.7 V at 1100 mA/cm^2, humidified operation and 800 mA/cm^2, unhumidified operation (Figure 7); SOFC: 0.78 V at 800 mA/cm^2) and multicell stacks are under construction. Thus, the key technological challenge is to reduce the size, weight, and cost of the bipolar separator plates and gas manifolds. Current contractors include Texas A&M University and Lynntech, In. (PEM) and Allied Signal (SOFC).
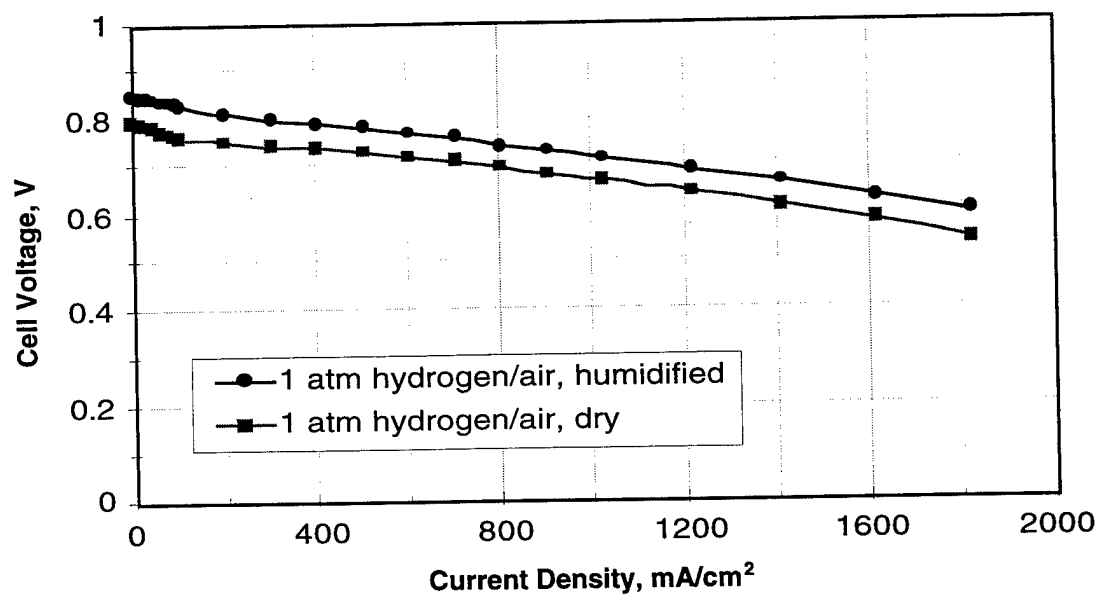
Figure 7. Recent performance of a 5 cm^2 hydrogen/air proton exchange membrane fuel cell operating at 60°C and 1 atm total pressure (Texas A&M University).

ARL ENERGY STORAGE PROGRAM

S. Gilman and M. Salomon
Electrochemistry Branch
Chem/Bioscience Division
Army Research Laboratory
Ft. Monmouth, NJ

Introduction

The ARL energy storage program is oriented toward the technology of lithium batteries, electrochemical capacitors and miniature fuel cells. The relative advantages and disadvantages of these components are shown in the table. Lithium batteries provide good energy density (improvements to the 400 Wh/kg level are foreseeable) and cannot be excelled for low temperature operation and fast startup and throttling. Major disadvantages are the high cost of primary batteries and the inconvenience of recharging under battlefield conditions. Small fuel cell systems, when designed for longer missions, can probably provide several times the energy density of batteries and low operating costs, but may not be useful for those Army communications missions which require extremely low temperatures (without ancillary heaters) and rapid startup. Electrochemical capacitors store modest amounts of energy but can provide power densities one to two orders of magnitude greater than the other two components and will find application in load leveling of those components.

Primary Lithium Batteries

Primary batteries have always been a preferred power source for Army communications under battlefield conditions. The Li/SO_2 battery, introduced by ARL in the early 1980s has provided superior performance, but has never achieved the commercial/low cost status desired by the Army. Li/MnO_2, under advance development of CECOM appears to be one candidate for future replacement of Li/SO_2. ARL is exploring $Li/(CF)_x$ as an alternative. The effort has two thrusts: the development of higher power density configurations than that of commercial cells (with Rayovac) and the preparation of low temperature fluorinated carbons (with U. of Grenoble) which should have higher ionic nature than commercial $(CF)_x$.

Rechargeable Li (Ion) Batteries

The Army now attached high priority to the development of a high performance rechargeable battery to accomplish cost savings in communications training. The most advanced "rechargeable Li" battery is the "Li-Ion" battery in which carbon serves as the host for Lithium fr the purpose of enhancing user safety. With present formulations, energy densities are only 2/3 that of the Army's present primary battery (Li/SO_2, 175 Wh/kg) with limited low temperature capability and big temperature stability. Wide acceptance within the Army for "realistic" training and future battlefield "distributed power" (when used with fuel cells, thermophotovoltaic generators or other larger primary sources), probably requires rapid recharge capability and improved discharge performance. ARL is continuing basic research on electrolytes and cathode materials (begun in the early 1970s) which has already contributed to present Li-Ion formulations. A more applied effort of developing low temperature, thermally stable electrolytes for an ARPA TRP program (with SAFT) was begun last year and has resulted in the discovery of an electrolyte additive to enable the use of imide and methide salts without the corrosion of cell current collectors.

The use of solid polymeric electrolytes may provide a doubling of the energy density of both rechargeable and primary Li batteries. ARL has had an R&D effort in this area for a number of years and has participated in ARPAs program to develop flexible manufacturing methods for Li/polymer batteries. The present ARL program includes SBIR Phase II contracts with Technochem Co. and Covalent Associates which are scheduled to produce prototype cells in FY 97. The Technochem contract includes the synthesis of new imide and methide salts for both solid

and liquid electrolytes. The covalent contract features the development of inorganic/organic composite electrolytes.

Electrochemical Capacitors

Two types of electrochemical capacitors have been proposed over the years. "Double Layer" capacitors usually comprise high area carbon and sulfuric acid, potassium hydroxide or an organic electrolyte. These will probably be most appropriate for the large capacitor banks needed for acceleration and dynamic braking of Army electric-drive vehicles and for engine starting of more conventional diesel-powered Army vehicles. "Pseudocapacitors" usually involve the use of hydrogen adsorption elements (Pt or Pd) or of superficially hydrogenated transition metal oxides (crystalline RuO_2, IrO_2) with sulfuric acid. The ARL program has resulted in the discovery that amorphous forms of RuO_2 can provide twice the energy density of the crystalline variety previously known (capacitance of 760 F/g) probably because it permits bulk hydrogenation of the material. Prototype capacitors made with the new material provide the highest energy and power densities yet reported for electrochemical capacitors. We see this as very attractive technology for use in emerging Army and civilian burst communications applications where the relatively small size of devices will allow the use of a higher cost material than carbon.

The continuing ARL program on capacitors (particularly ARPA/ASTO - funded) has two thrusts: 1) the further development of RuO_2 prototype capacitors and 2) the development of improved carbons and organic electrolytes for double layer capacitors.

Miniature Fuel Cells

Small fuel cell systems may be used to directly power electronic and small electrical equipment for the individual soldier or to recharge lithium batteries for those applications. The most appropriate technology for that purpose now appears to be hydrogen or methanol - fueled PEM technology. ARL has been participating in and complementing ARPA and ARO-funded programs which have the goal of developing such technology.

In the area of H_2/PEM fuel cells, ARL has been particularly concerned with achieving very lightweight high power density stacks for 50-200 W service. For small units, it would be vary advantageous to avoid the need to provide ancillaries for membrane humidification, heat removal, air convection, etc. An effort was initiated with Dupont to modify NAFION to retain good conductivity under low Rh conditions. Samples with twice the conductivity under normal conditions have been prepared and are under evaluation. An SBIR program was initiated to develop lightweight materials and designs for fuel cell stacks. The internal program includes the development of technology for "printing" monopolar fuel cell arrays on a single sheet of polymer.

In the area of methanol/PEM fuel cells, the ARL internal effort has concerned itself with electrocatalysts. Recently completed work concerned evaluation of catalytic properties Vs catalyst morphology for a wide range of Pt/Ru catalysts prepared by thermal decomposition of salts.

RELATIVE CHARACTERISTICS OF ELECTROCHEMICAL ENERGY STORAGE DEVICES

	Li Batteries	Electrochemical Capacitors	Small Fuel Cell Systems
Energy density, Wh/kg	*100-300*	*<10*	*>400*
Power density, W/kg	*<100*	*>1000*	*<100*
Purchase cost	medium	low	high
Cost/Whr	primary: high rechargeable: low	low	*low – very low*
Operating temperature	*full ambient*	*full ambient*	high ambient
Startup	*fast*	*very fast*	slow

LIGHTWEIGHT PEM FUEL CELL STACK DEVELOPMENT SBIR PROGRAM

OBJECTIVE

● To develop lightweight monopolar or bipolar hydrogen-fueled stacks using novel materials and designs

● Stack power in the 50-150 watts range, in support of CECOM's current development goals

STATUS

● Eleven (11) Phase I six-month contracts ($70 K each) have been completed (4/95-10/95)

● Procurement packages prepared for multiple Phase II awards

CONTRACTORS

● Fiber Materials Co.
● A.F. Sammer Corp.
● Lyntech Inc.
● H Power Corp.
● Analytic Power Corp.
● Energy Partners Inc.
● Giner Inc.
● MER Corp.
● EIC Labs
● Electrochem Inc.

RECHARGEABLE LITHIUM BATTERIES

Army Need

- Performance similar to Li/SO$_2$ primary + rechargeability for realistic training, distributed power

Present Status

- Li-Ion (liquid organic electrolyte) batteries under advanced development with energy density ~2/3 primary Li (~110 Wh/kg), with low temperature, and storage life limitations

Research Needs

- Improved organic electrolytes for higher power densities, lower operating temperature and better storage
- More energetic anode and cathode materials for higher energy densities
- Solid (polymer) electrolytes for even higher energy densities (better packing efficiencies) and lower manufacturing costs

RECHARGEABLE Li-ION BATTERIES
ARL R&D PROGRAM

● Prior ARL research has contributed to the composition of the present baseline cathode and electrolyte

● Improved Electrolytes

- Need higher ionic conductivity (for higher power density, lower operating temperature), greater thermal stability (for better storage, safety) and good environmental acceptability.

- Continuing generic basic research to identify more soluble and dissociative salts, new solvents, and develop predictive theory

- Screening of new electrolytes for ARPA/SAFT TRP program begun in FY 95 - continuing in cooperation with CECOM COE

● Alternative Anode and Cathode Materials

- Needed for higher energy and density

- Some exploration of new cathode materials (e.g., Li_xCuO_2)

- Exploration of inorganic binders for Carbon (with Johns Hopkins University)

Li/POLYMER BATTERIES
ARL R&D ACTIVITIES

Internal

- Past: Exploration of electrolytes based on PEO, PAN
- Formulation/evaluation of PMM, PVDF and PVDF/ceramic gels
- Studies include conductivities, physical properties, thermal stability, electrode/electrolyte interfacial impedance, and demonstration of prototype cells

Technical monitoring of ARPA Contracts

Technochem Co. (SBIR - 4/95 to 4/97)

- Synthesis of new Li salts
- Formulation of gel electrolytes using new salts
- Development of prototype cells

Covalent Associates Inc. (SBIR - 4/94 to 10/96)

- Development of gel electrolytes using Li-substituted molecular sieves
- Development of Prototype cells

PRIMARY LITHIUM BATTERIES

BACKGROUND/ARMY NEED

● Li/SO$_2$, introduced in early 80's is not low cost, commercially-based

● Prior ARL research led to battery chemistries (Li/SOCl$_2$,Li/SO$_2$Cl$_2$) with energy densities >2X Li/SO$_2$ (350 Wh/kg), but these are not low cost, commercially-based

● Li/MnO$_2$, advance-developed by ARL/CECOM is commercially-based and may be lower cost but other chemistries might provide better performance and increase vendor competition

Research Needs

● Alternative cathode materials (e.g., (CF)$_x$, improved MnO$_2$) for higher energy density, commercial base)

● New polymer electrolytes (for even higher energy density, body-conformable battery design)

PRIMARY Li$(CF)_x$ BATTERIES

- Cell discharge reaction:

  $$xLi + (CF)_x \rightarrow xLiF + xC$$

- Practical energy densities greater than 1.5 x present Li/SO_2 are possible (has 2x theoretical energy density of Li/SO_2)

- Commercial base exists for small low power density batteries with excellent storage characteristics (Eagle Picher, Rayovac, Panasonic)

- Present 15-month contract with Rayovac covers development of cells with higher power density

- Subcontract with University of Grenoble deals with fundamental improvement of $(CF)_x$

- ARL internal effort deals with evaluation of $(CF)_x$ preparations, thermal stability and storage life of cells (using microcalorimetry)

ELECTROCHEMICAL CAPACITORS

Army Need

● Energy storage component with power and energy densities >3 kW/kg and >15 Wh/kg, respectively; very long cycle life and very rapid recharge for burst communications, electric drive vehicles (ARPA & Army), and engine starting

Available Technology

● Batteries cannot provide the extremely fast recharge and very long cycle life that is required

● Low voltage commercial electrochemical capacitors are available with low energy and power densities

ARL Approaches

● Pseudocapacitor R&D for communications applications

● Double layer capacitor R&D for other applications

Background

RuO_2 as an electrode material for EC capacitors

Conway, Raistrick, Sierra Alcazar et al.

Prepared by thermal decomposition of $RuCl_3.xH_2O$ at <u>300 °C</u>

<u>Crystalline phase</u>

High conductivity.

High capacitance: ≈ 380 F/g (for 130 m^2/g) or 300 μF/cm^2 (vs. 20-30 μF/cm^2 for double-layer capacitance)

<u>Fast redox reaction at surface sites</u>

$$RuO_2 + \delta H^+ + \delta e^- \leftrightarrow H_\delta RuO_2 \qquad 0 < \delta < 1$$

ARL Discovery

<u>Low temperature formation process:</u> sol-gel process

Hydrous ruthenium oxide ($RuO_2.xH_2O$)

<u>Amorphous phase and powder form</u>

High conductivity

High capacitance: 760 F/g

Fast redox reaction into the <u>bulk</u> of $RuO_2.xH_2O$ ($0 < \delta < 2$)

Crystal Structure of RuO$_2$

	Preparation Method	Crystal Structure
RuO$_2$	Thermal decomposition of RuCl$_3$.xH$_2$O in H$_2$O at 300 ^{o}C	Crystalline
RuO$_2$	Ruthenium alkoxide in organic solvent as precursor	Amorphous, T < 200 ^{o}C Crystalline, T > 200 ^{o}C
RuO$_2$	Pulse laser deposition	Amorphous, T$_S$ ≤100 ^{o}C Crystalline, T$_S$ ≥200 ^{o}C
RuO$_2$.xH$_2$O	Aqueous sol-gel process	Amorphous, T ≤150 ^{o}C Crystalline, T ≥175 ^{o}C

FUEL CELLS

Army Need

- Small, lightweight power source with energy density >400 Wh/kg for lengthier individual soldier applications (direct power or with rechargeable batteries)

Present Status

- Present hydrogen PEM fuel cell systems require miniaturization

- Fully acceptable electrocatalysts and PEM's do not exist for methanol fuel cells

Research Needs

- Dehydration-tolerant ion membrane for hydrogen fuel cells

- Lightweight materials and technology for hydrogen fuel cell stacks

- Better electrocatalysts and ion membranes for methanol fuel cells

METHANOL/PEM FUEL CELLS

- Methanol/PEM fuel cells offer the possibility for relatively simple, small high energy systems

- ARL is participating in the ARPA Direct Methanol fuel cell program which targets "individual soldier" application

- Internal work has been oriented toward electrocatalyst characterization
  - Mechanism of methanol/O_2 interaction at cathodes
  - Preparation/characterization of Pt/Ru catalysts
  - Evaluation of adsorbates for selective poisoning of methanol oxidation at O_2 electrodes

- Research (MRCP) programs established at Johns Hopkins University
  - Physical chemistry of methanol/NAFION interactions (Prof. T.A. Barberi)
  - Electrochemical STM studies of methanol electrocatalysts (Dr. R. Srinivasan)

DEVELOPMENT OF IMPROVED MEMBRANES FOR H$_2$/AIR FUEL CELLS

OBJECTIVE

● Preparation/evaluation of sulfonated fluorocarbon membranes with high protonic conduction under low RH, high current density fuel cell conditions

CONTRACTOR

Dupont

APPROACHES

● Use of low equivalent weight monomer

● Use of irradiation (with/without) added reagents to introduce functional groups and to induce cross-linking

● Measure conductivity, water absorption

● Construct/evaluate small fuel cells

ACCOMPLISHMENTS

● A number of new membranes have been prepared with higher conductivities under room temperature, high RH conditions

● Evaluation under low RH conditions in process

U.S. ARMY CECOM BATTERY ARSENAL

H.A. Christopher
U.S. Army CECOM Battery Arsenal
U.S. Army Communications-Electronics Command Research
Development Engineering Center
Ft. Monmouth, NJ

Introduction

The end item products of CECOM's Research, Development and Engineering center range from large, ground based Satellite Communication and complex Command & Control systems to small, manpack portable electronic devices such as night vision goggles and radios. There are about 700 of these small Communication/Electronic devices in the field or on the drawing boards today. They are all designed to operate on battery power and today there are over 300 different battery types (mostly primary/throwaway types) supplied to the field to support these end items. This battery proliferation contributes significantly to both the logistics and cost burden of the Army. Last year CECOM bought about $48M of these batteries representing more than half of the Army Material Command's FY-95 $77.2M battery expenditure (Figure 1).

To reduce the proliferation/cost problem we are working with equipment developers to encourage the use of commercial, off-the-shelf batteries (first priority) or one of the five standard Army battery configurations we have selected based on their present demand/sales volume. The largest and most popular standard battery today is the BA-5590 primary Lithium/sulfur dioxide battery driven by the requirements of the SINCGARS (manpack) radio. This battery configuration also serves as the power source for over 50 other equipments covering power demands ranging from only a few watts-continuous duty to over 300 watts-burst. The latter achievable today only with the Nickel cadmium or Nickel Metal Hydride "5590" analogs.

Over the past several decades the power requirements of new CECOM equipments has increased exponentially (Figure 2), and we have developed and fielded higher performance batteries to meet these needs (Figure 3). During the last several years cost has become a relatively higher priority in the user community. This has resulted in imposing the use of lower energy density rechargeable batteries with their attendant chargers for training missions against the desire of commanders who want to "train as we fight". The result is a user community with a list of unrealistic demands (Figure 4) and an unwillingness to consider trade-offs in convenience and performance against cost and related logistics issues (Figure 5).
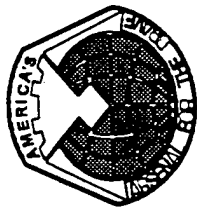
Primary Batteries

The Lithium/sulfur dioxide primary battery system took over ten years to develop before its initial fielding in the late 70s and has been further improved in each subsequent production contract. It is still a military-unique system and will be hard to beat as a war reserve, combat-ready power source (Figure 6).

During the 80s the Army spent several million dollars to complete the development of a family of lithium thionyl chloride analog primary batteries having early twice the energy content of their SO_2 counterparts. This system never got into production due to the lack of cost effectiveness over SO_2 and the concern for involvement with another military unique primary battery.

Today our focus is on the development of a dual-use lithium Manganese dioxide system with light weight, low cost, "pouch cell" prismatic packaging technology (Figure 7).

Additional Systems Under Consideration

Rechargeable Batteries
Hybrid Power Sources
Metal (Zinc)-Air Batteries
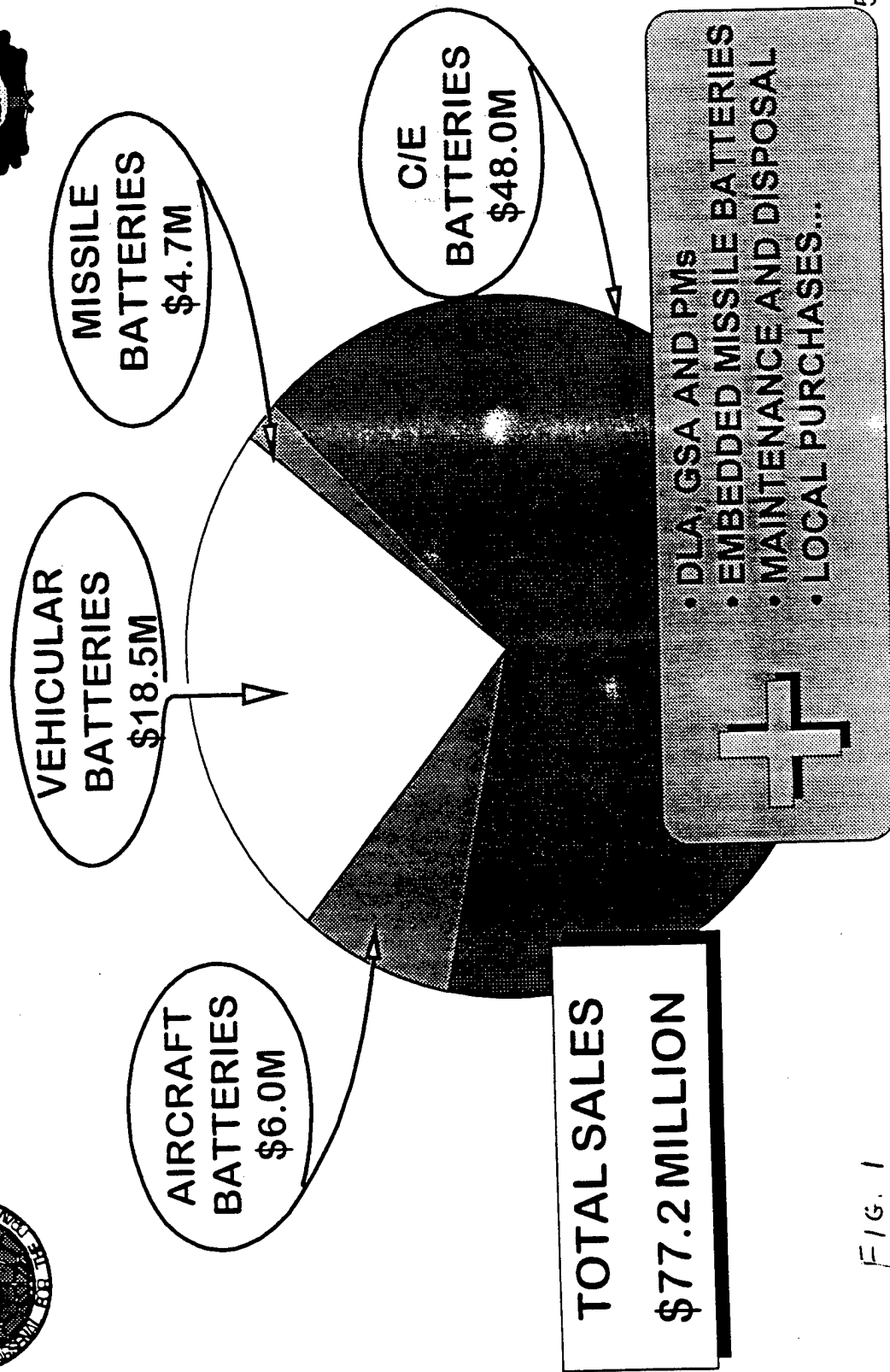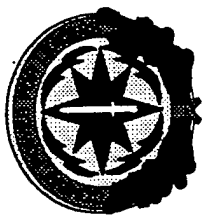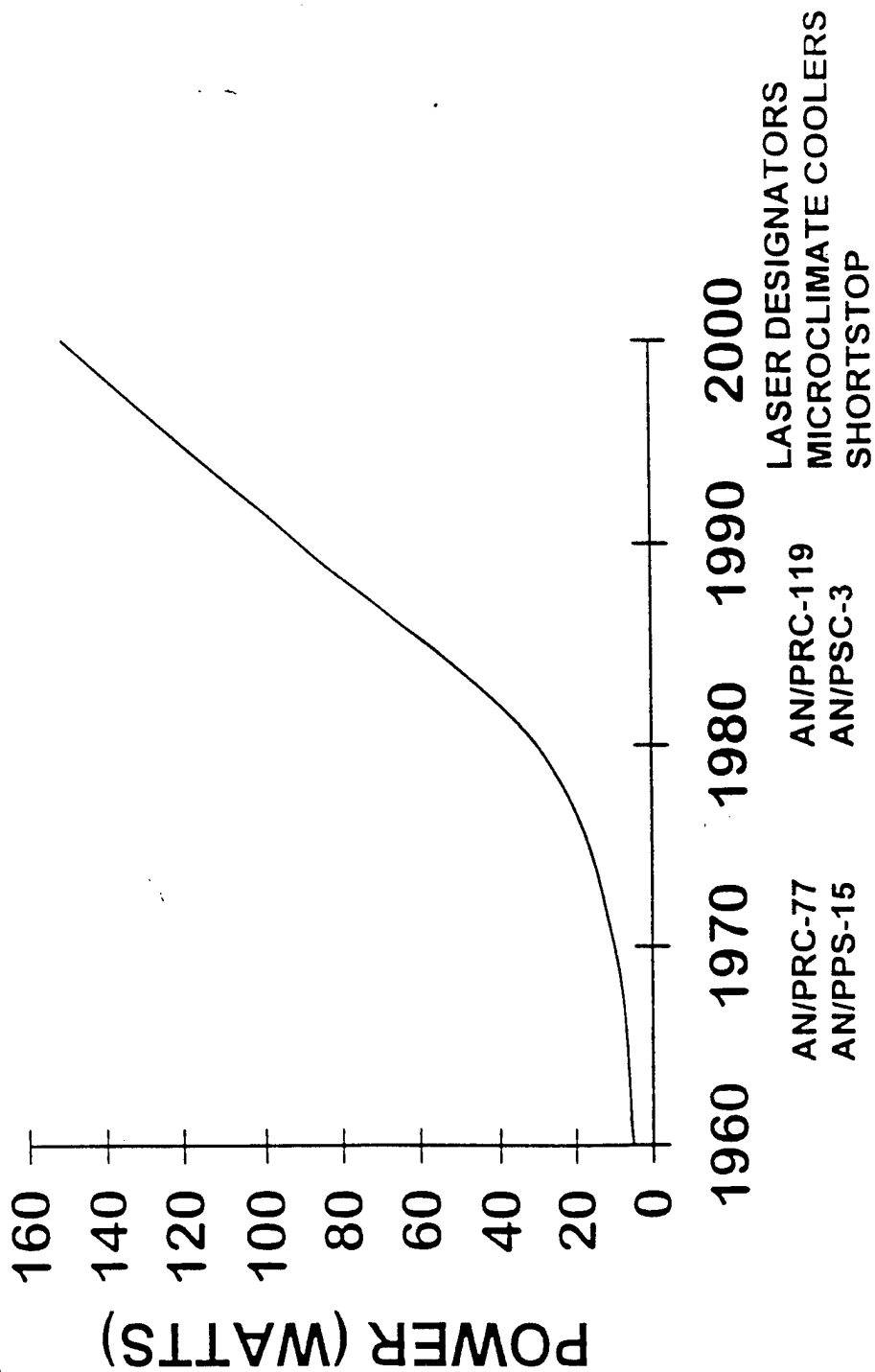Thermophotovoltaics

FY-95 AMC BATTERY SALES

MISSILE BATTERIES $4.7M

C/E BATTERIES $48.0M

VEHICULAR BATTERIES $18.5M

AIRCRAFT BATTERIES $6.0M

• DLA, GSA AND PMs
• EMBEDDED MISSILE BATTERIES
• MAINTENANCE AND DISPOSAL
• LOCAL PURCHASES...

TOTAL SALES $77.2 MILLION

FIG. 1

5
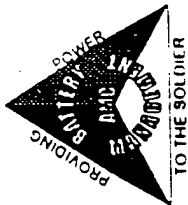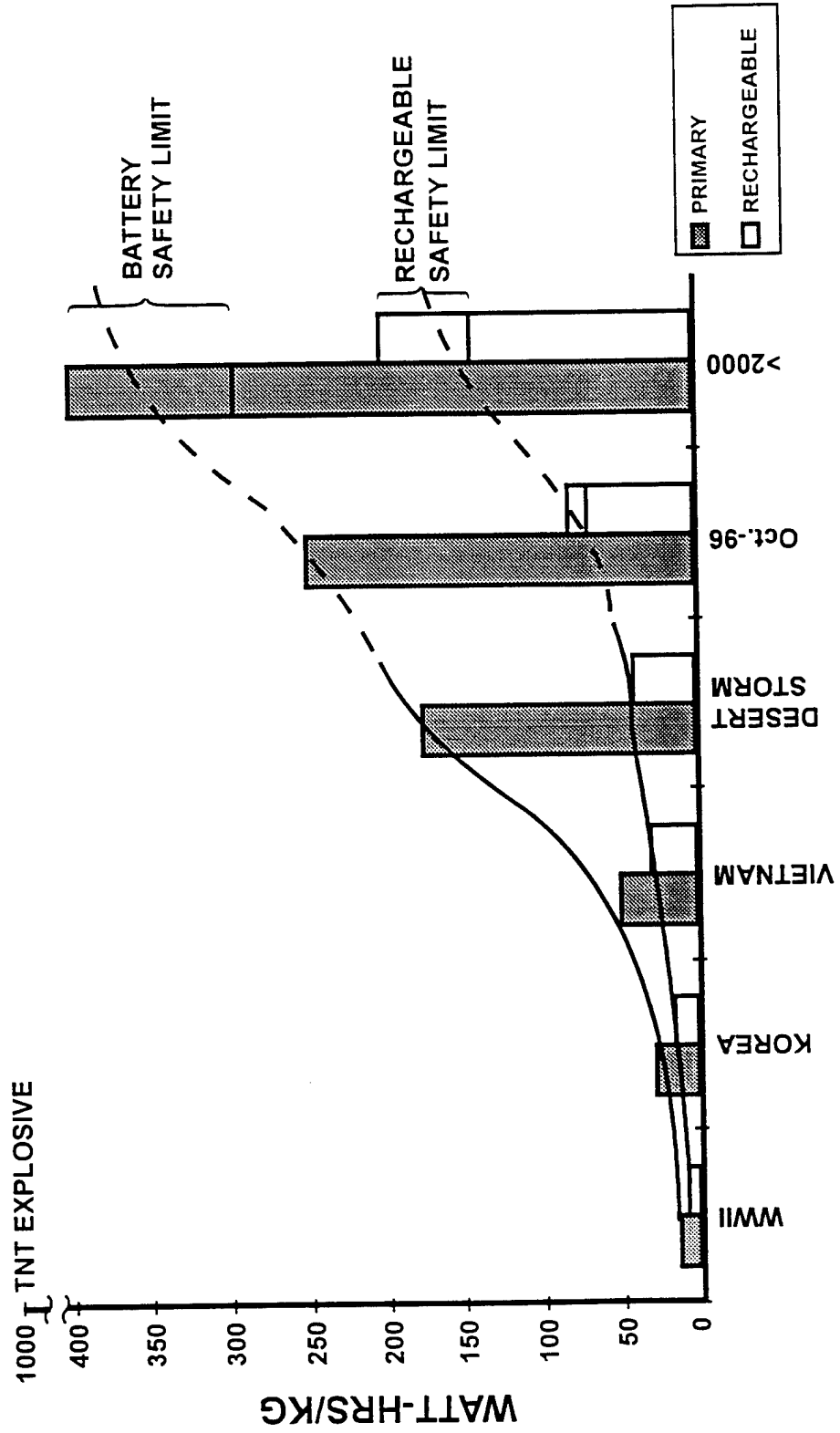
POWER CREEP

Fig 2

BATTERY EVOLUTION

FIG 3

USER PERCEIVED STATUS

TYPICAL COMMENTS FROM THE FIELD:

BATTERIES:

COST TOO MUCH

WEIGH TOO MUCH

DISPOSAL DIFFICULT

REPLACEMENT RATE IN VEHICLES TOO HIGH

COST TOO MUCH FOR TRAINING

POWER MANAGEMENT:

EQUIPMENT POWER USAGE TOO HIGH

POWER CONSUMPTION IS EXCEEDING CAPABILITY TO SUPPLY WITH BATTERIES OR GENERATORS

>50% OF BUDGET IS SPENT ON POWER

SYSTEM IMPERMEABLE TO USER / IDEAS
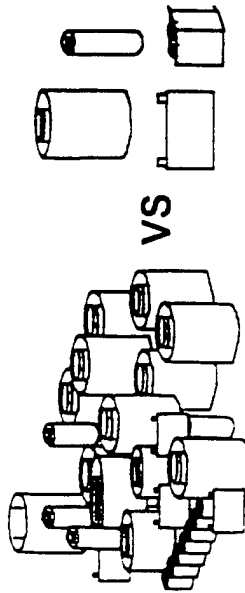
FIG 4

Generic Requirements

Longer Cycle Life

25 uses → 50-75 uses

Fewer Size & Types

vs
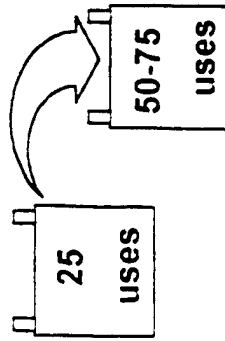
Environmentally Friendly and Safe Chemistries

Solar NI-MH Lithium NiCad Other

Lower Cost

Maintenance Free

COTS/Multi-use

Fewer Voltages

1.5 v
3.6 v
7.2 v
9 v
12 v
24 v
28 v

vs

3 v
6 v
12 v
24 v
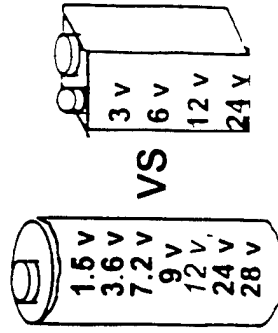
Smaller & Lighter

Standardize

FIG. 5

Lithium Sulfur Dioxide

Features

- High Performance 75 wh/lb. @ 25 w/lb.

- Excellent Shelf Life

Status

- Standard Family fielded 1980

- Complete Discharge Device

- State-of-Charge- Meter fielded

- State-of-Charge- Indicator Developed/ Proven

Hurdles

- High Cost

- No Commercial Market

(Military Unique)

FIG. 6

Lithium Manganese Dioxide

Features

- 1.5 x Li/So_2 Energy
  or
  2x Li/So_2 Power

- Light Weight, Low Cost
  Pouch Cell Construction

- Commercial Chemistry

Status

- "Best Value"
  and/or
  1/2-Size BA-5590

- State-of-Charge-
  Indicator

- Bids Expected on
  on Multi-Year Buy

- 25 WH D-Cell Developed

- 21 CLW/Gen II Demos
  1996, 1998

Hurdles

- Low Temperature

- Pouch Shelf Life

- Impurity Effects

FIG. 7

BATTERY COMPARISON

EQUIPMENT	MISSION TIME (HRS)/(BATTERY TYPE)			
	PRIMARY	RECHARGEABLE		
		NiMH	NiCAD	Li-ION
SINCGARS	24 (BA-5590)	8 - 12 (BB-390A)	4 - 6 (BB-590)*	N/A
AN/PRC-126	60 (BA-5588)	27 (BB-388)	16-19 (BB-588)*	N/A
TWS	5-12 (BA-5847A)	N/A	N/A	3-7.5 (BB-2847)

* WILL BE REPLACED BY NiMH VERSION

FIG. 8

Rechargeable Battery Comparison (BB-590 Configuration)

	Nicad	NMII	Lithium-ion FatD cell	Lithium-ion 18650 cell
Nomenclature	BB-590/U	BB-390/U		
Watt-Hours (WH)	48	86	130	100
Amp-hours (AH)	2.2	3.6	4.5	3.4
Voltage Range(volts)	26-20	26-20	32-20	32-20
Cell # and type	20 CsD	40 (A)	8 (Fat D)	24 (18650)
Weight (lbs)	3.7	3.8	3.0	3.0
Charge time (hours)	1-7	3-7	3	2
Capacity loss/month(%)	20	30	10	10

FIG 9

FUEL CELL WORK AT LANL AND COMMENTS ON
FUEL CELL BASED INEXPENSIVE PORTABLE POWER SOURCES

Dr. Shimshon Gottesfeld
Los Alamos National Laboratory
MEE11-Electronics Research Group
PO Box 1663
MS D 429
Los Alamos, NM 87545

The fuel cell core research program at LANL has been involved in polymer electrolyte (PEFC) R&D for more than 10 years and has thus become a center of expertise in this field of science and technology. The work of the group at this point in time is divided into efforts on reformate/air fuel cells, supported by DOE/OTT and DOE/OUT, and direct methanol fuel cells, supported by DOE for potential transportation applications and by DARPA for portable power applications.

In the direct context of the main subject of this Workshop, we have recently developed an air breathing fuel cell "stackette', fueled from a small metal hydride canister, which provides an interesting basis for a power source of properties close to 14W/60 Whrs, of volume and weight which could seriously be considered for, e.g., a lap top computer. This system has been patented by LANL (Mahlon Wilson). It takes advantage of some advanced membrane/electrode assemblies based on very thin membranes as recently developed by W.L.Gore, to achieve very stable performance under the simplest (least demanding) conditions of air breathing (no forced flow) and no external supply of humidity. Work on this system consisting of small scale air breathing PEM fuel cell combined with a small metal hydride canister (total dimensions already quite close to what is required for packaging into a lap top case), has provided us with a pretty good idea on the ultimate simplicity and potential for low cost of such portable fuel cell systems and on how close they are already to compelling demonstration and subsequent possible implementation.

Having stressed the most direct origin of our belief in the potential of fuel cells as low cost/high performance portable power sources, let's return to a brief discussion of ongoing work at LANL in this general field of R&D.

Hydrogen and Reformate/Air Fuel Cells

The work consists of R&D and testing efforts based primarily on the membrane/electrode technology developed at LANL which enables very high performance with ultra-low catalyst loadings. Loadings as low as 0.1 mgPt/cm2 on the cathode and one fifth of that on the anode are sufficient to obtain areal power densities of 0.5W/cm2 of membrane area in operation on neat hydrogen and air. In portable power applications, hydrogen/air cells will need such small amounts of Pt that the cost of the catalyzed membrane will be very small (of the order of cents per watt, considering lower cost, non-fluorinated proton conducting membranes which are being developed now at several places including, e.g., Hoechst, and that could provide low-cost viable alternatives to PFSA membranes for such applications.

Recent efforts at LANL in the field of PEM fuel cell R&D have been devoted to:

* CO tolerance of the anode

* Low Cost, Manufacturable Fuel Cell Hardware Components

* Novel humidification schemes, including operation with no external humidifcation

We have recently demonstrated that tolerance to CO levels as high as 600 ppm in hydrogen feed streams can be achieved in PEM fuel cells by using PtRu anode catalysts of somewhat higher loadings and increasing the cell operation temperature to 120^0C. This is not necessarily relevant to portable power applications, unless the hydrogen is to be derived, for example, from reforming of liquid fuels, rather than from stored pure H_2.

We have performed recently a 2000 hours life test of a hydrogen/air PEFC of 100 cm^2 active area with low loading LANL membrane/electrode assemblies (MEAs) and with the hardware for the bipolar plates and for the flow fields all based on 316 stainless steel foils and screens -- off-the shelf sheets and screens, just cut and punched (no machining). The test revealed no loss of conductivity in either the metal components or the membrane of the tested cell after continuous operation for 2000 hours. This result reveals further important potential for simplification of PEFC stack configuration and mode of manufacturing. Although the use of metal hardware may pose some question in portable power applications, it is possible that some higher conductivity and mechanical advantages will enable higher volume power densities and, consequently, comparable weight power densities to those achieved with graphite based stacks. At this point, however, graphite/plastic composites, machined and, more recently, molded, have been considered the primary materials of choice for PEM fuel cell bipolar plates. The latter require some improvement in conductivity, particularly surface conductivity, and improved mechanical flexibility to facilitate failure free stack assembly.

As to effective and simple humidification schemes for hydrogen/air cells, it has been mentioned above that stack operation without any external humidification has been demonstrated by us for air breathing stacks developed for portable power. The technology development required to achieve this important feature has been the one mil thick ionomeric membranes and MEAs, as developed recently by Gore.

Direct Methanol Fuel Cells (DMFCs)

Comparable evaluations of hydrogen/air and methanol/air systems for portable power applications shows the opportunity in both cases to exceed 100 Wh/Kg of system weight with additional developments in each of these fuel cell technologies (see my comments attached on the relevant future R&D efforts required). The main advantage of the DMFC is the higher energy density of the fuel. The main relative disadvantages at the time this summary is being written are "leaky" ionomeric membranes (excessive cross-over) and less established performance reliability/reproducibility for a DMFC stack vs, a hydrogen/air stack. The work on DMFCs at LANL preceding the DARPA-sponsored work at LANL on this subject, has concentrated on potential transportation applications (sponsored by DOE/OTT). The stress has thus been maximizing performance, and the way to achieve that target has been hiking the temperature of the DMFC over 100°C. This turned out to be possible with ordinary Nafion membranes, because the anode side of the membrane is kept in contact with a methanol/water liquid mixture at such elevated temperatures, keeping the resistivity of the membrane low even at temperatures as high as 130°C. Methanol/oxygen and methanol/air cells have been demonstrated to yield under such conditions power densities of 400 and 250 mW/cm^2 of membrane area, respectively. Such performance has generated significant renewed interest in the prospects of this directly liquid-fed fuel cell as a primary power source not only for portable power but also for transportation applications. In fact, overall energy conversion efficiency, overall system power density and energy density and overall system cost seems all to be rather close for a system based on a DMFC and a system based on a methanol reformer and a reformate/air fuel cell for transportation applications.

Summary

From the experience accumulated at the Fuel cell Core Technology R&D program at LANL, there seems to be a very good basis for the hope to manufacture small scale fuel cell power sources for portable power (10W - 100W range with 5-10 hours mission) for less that 1 $/Wh and better than 100 Wh/kg. Both hydrogen/air and methanol/air systems should be considered. Comments on further R&D efforts required have been outlined below.

I. Hydrogen/Air Fuel Cells

(1) **Performance**:   The main barrier to competitive performance of hydrogen fueled PEM fuel cells as battery replacements has been limited hydrogen storage capacity in safe form. To achieve competitive energy densities (in excess of 200 Wh/Kg for missions of ten hours) the most important development required in the field of hydrogen/air PEM fuel cells is hydrogen storage with weight percent hydrogen of about 4%. To satisfy, at the same time, safety requirements, storage in solid state is preferrable to gaseous storage at high pressure. Storage in the form of a chemical system for generation of hydrogen (e.g., water + hydrogen releasing solid) is probably an intermediate priority. As a comment, it should be noted that some relaxation of the storage density requirement could be achieved by an increase of the net power density of the PEM fuel cell stack beyond 100 W/liter in air breathing or forced 1 atm air convection mode.

(2) **Temperature range**: A weak aspect of the PEM fuel cell is the very limited performance below the water freezing point. This is caused by problems associated with water freezing in various parts of the system, but the most fundamental problem has to do with the drop of protonic conductivity in the membrane electrolyte with temperature. It is suggested that a long-term effort should be considered to try to improve membrane conductivity at temperature below the water freezing point. Design of new ionomers with enhanced proton mobility at T< 0 deg C could be based on (I) fine tuning of properties of PFSA membranes (e.g., lower EW) taking advantage of the limited life requested in these applications, or more radical changes, such as imbibing in liquid electrolyte (solution for one-time-operation only).

As long as an alternative membrane material for T< 0 deg has not been provided, effective modes of start up from very low temperature have to be demonstrated. This is not considered a very touhg problem, but should be demonstrated for each start upode proposed to satisfy "Start-Up" requirements.

Comment: Freeze-rethaw cycling without resulting loss of PEM stack performance under ordinary opertion conditions has been demonstrated for some cell/stack configurations.

Direct Methanol Fuel Cells:

Rapid Start Up(Short/Medium): Because of the low power of the DMFC at temperatures of 25 deg C or below, bringing the cell temperture up by cell shorting could be too slow. Solutions are required, for example temperary operation on hydrogen (from hydride storage) or on hydrogen/methanol mixtures, catalytic methanol/air recombination at the cathode catalyst.

Performance (Medium): Cross-over of methanol through the membrane electrolyte has been identified as the most severe present day defficiency. Membranes of lower methanol flux AND satisfactory protonic conductivity (such as to suffer only minimal, or zero lowering in voltage effciiency) are the highest priority materials reseacrh target.
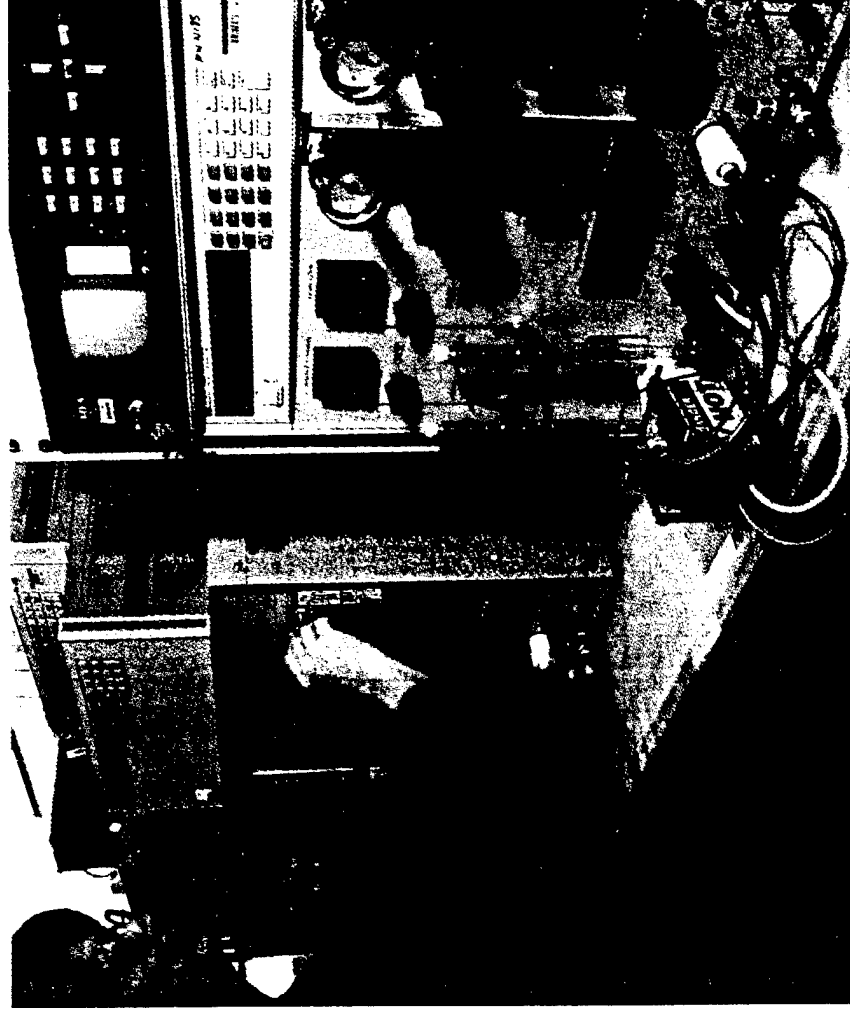
Reliability (Medium): Questions of performance stability are still open, to do with the stability of anode cathode catalysts as well as other electrode and membrane properties under DMFC operation conditions. The work required to answer these qeustions includes DMFC testing with effective diagnostics and development of alternative electrode materials and structures to enhance long-term stability and reproducible performance. Another key to achieving the "Reliability" requirements could be a "methanol stopping membrane" of sufficient protonic conductivity which could minimize those problems associated with methanol cross-over.

Cost: Lowering anode catalyst loading while maintaining performance is required to lower cost.

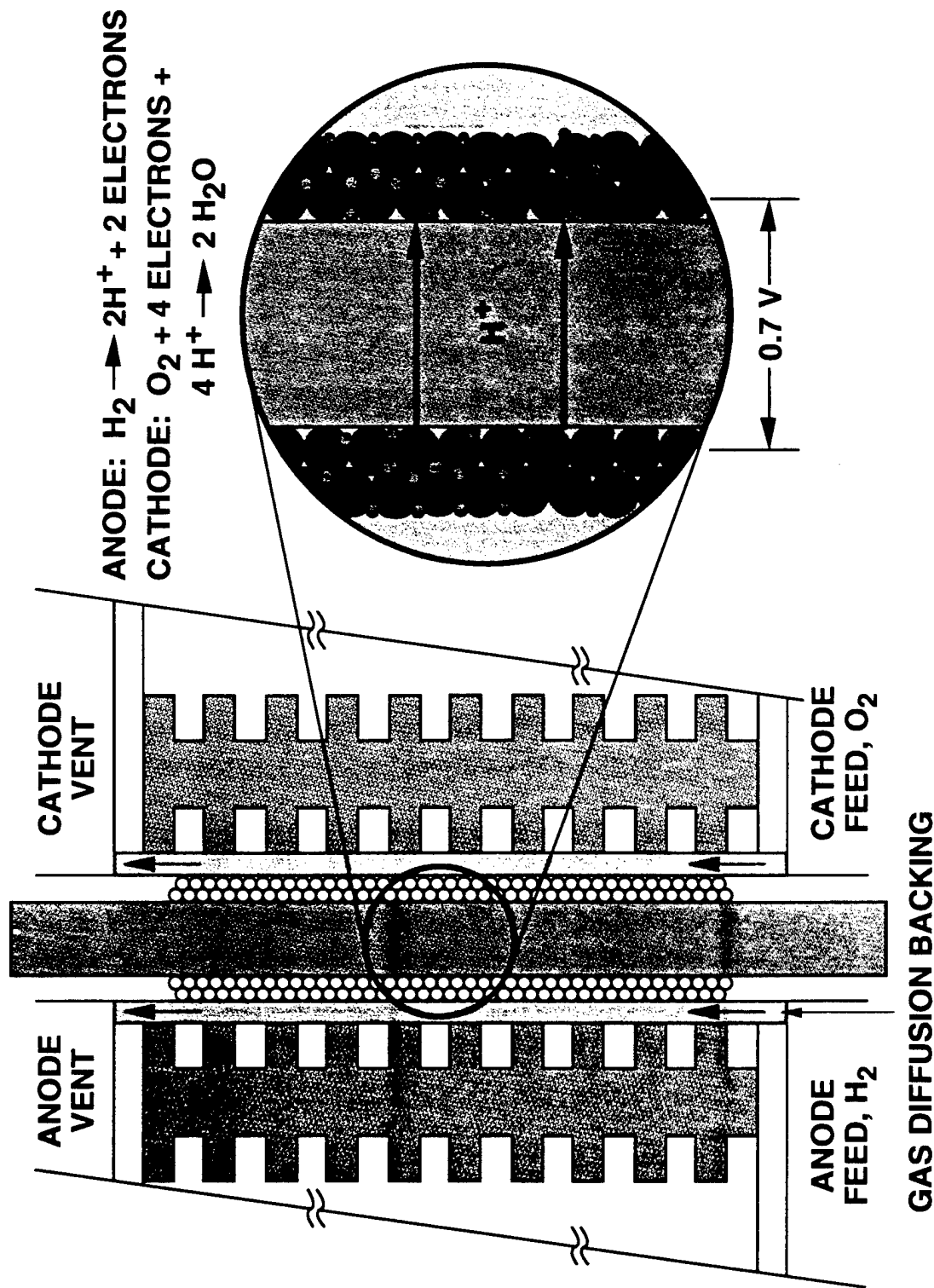**Temperature Range**: See discussion of a low T membrane for the PEM fuel cell, as well as Start-Up issues for the DMFC.

Fuel Cell Core Research Program

To conduct the basic and applied research necessary to bring polymer electrolyte membrane (PEM) fuel cell technology to the performance and cost levels required for widespread use in transportation

LOS ALAMOS

— ELECTRONICS RESEARCH

CROSS SECTION OF POLYMER ELECTROLYTE FUEL CELL

ANODE: $H_2 \longrightarrow 2H^+ + 2$ ELECTRONS

CATHODE: $O_2 + 4$ ELECTRONS + $4 H^+ \longrightarrow 2 H_2O$

0.7 V

H^+

CATHODE VENT

CATHODE FEED, O_2

ANODE VENT

ANODE FEED, H_2

GAS DIFFUSION BACKING

Three Generations of Catalyst Layers for Polymer Electrolyte Fuel Cells

IONOMER ■ **TEFLON** ○ **CARBON** ● **PLATINUM**

← 3 µm →

← 50 µm →

Pt Black/Teflon Bonded to Membrane 4 mg/cm^2

Pt/C/Teflon Catalyst Layer on Carbon Cloth Electrode; Hot Pressed to Membrane 0.5 mg/cm^2

Pt/C Catalyst Bonded to Membrane 0.15 mg/cm^2
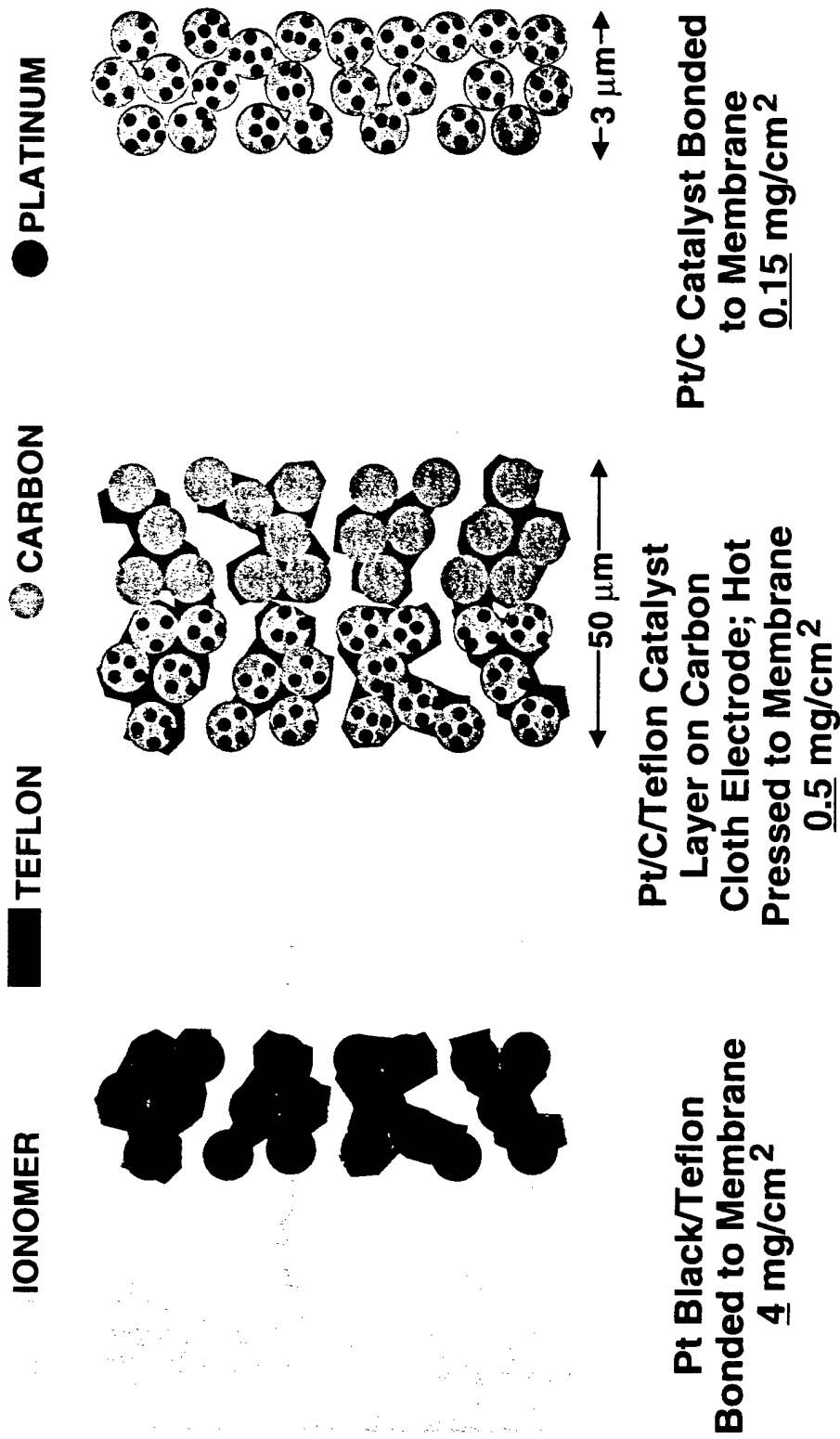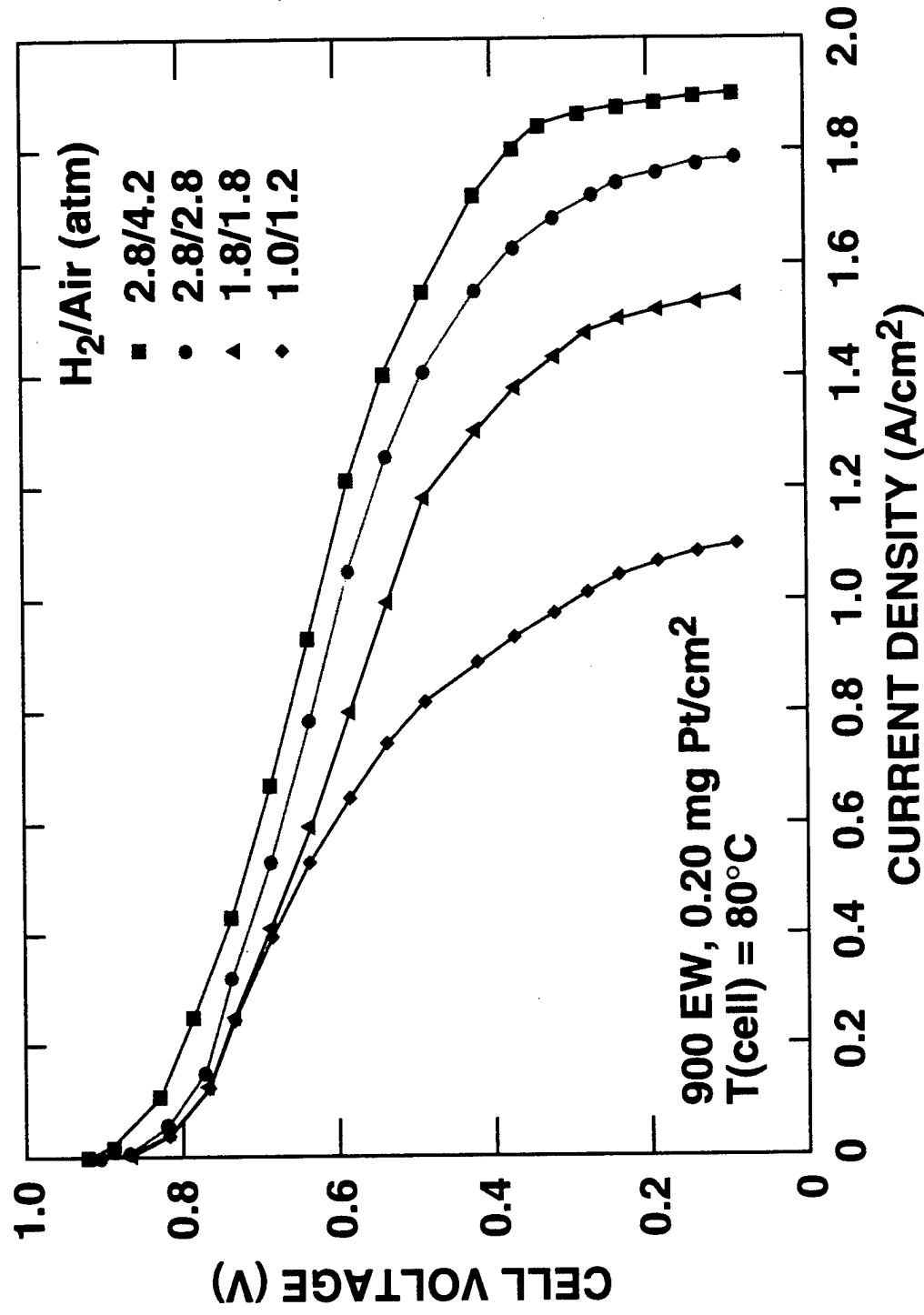
Air-Breathing Fuel Cell System

Stand-alone Fuel Cells with no auxiliary systems:

- No humidification
- No cooling
- No pressurization
- No forced reactant flows (hence "air-breathing")

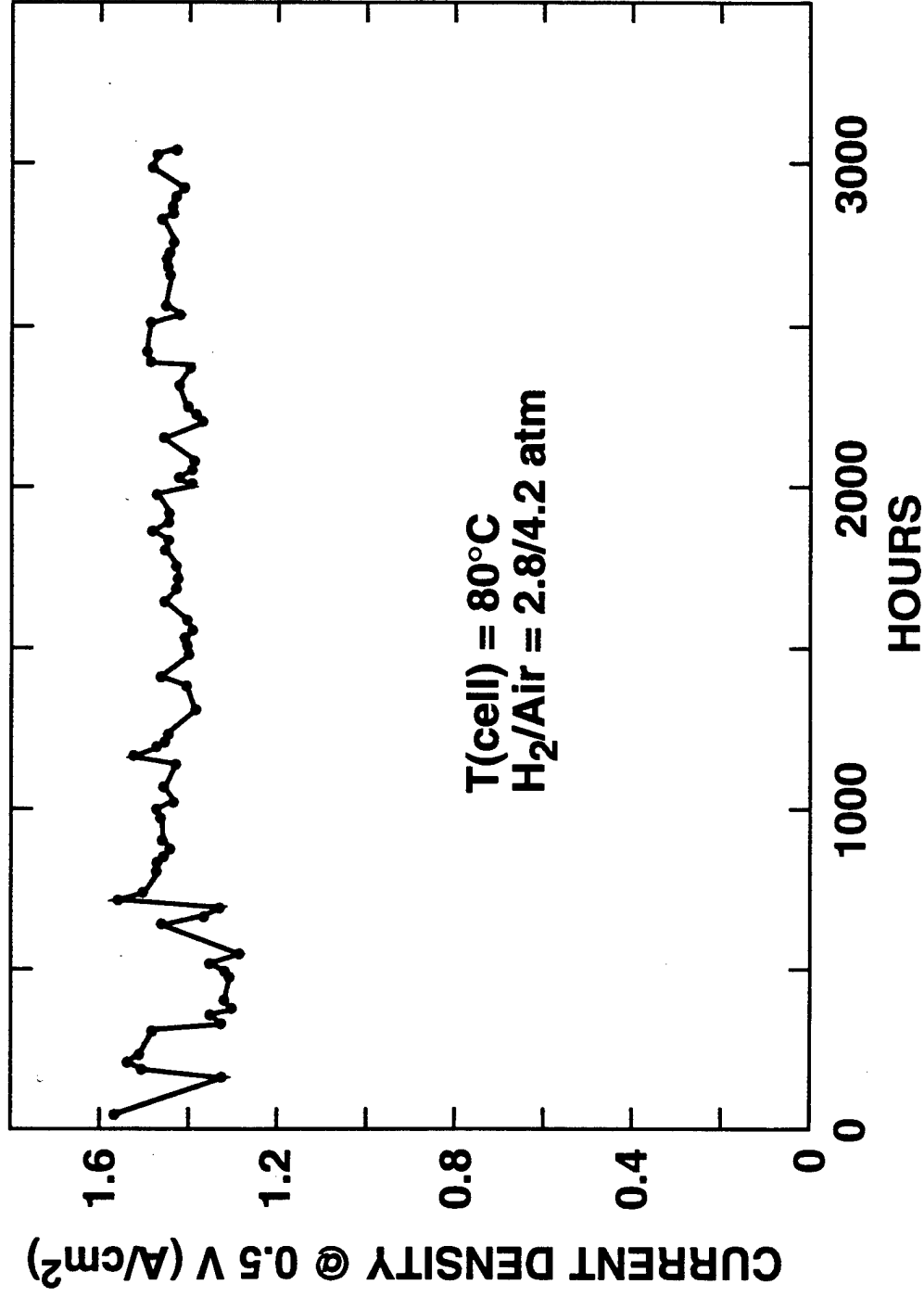## Power sources for battery-type applications that are:

- Simple (reliable)
- High energy density
- Quickly "re-chargeable"

12 μm Thick GORE-SELECT™ Membrane Performance of Fuel Cell

12 μm Thick GORE-SELECT™ Membrane Life Test

T(cell) = 80°C
H$_2$/Air = 2.8/4.2 atm

CURRENT DENSITY @ 0.5 V (A/cm²)

HOURS

0   1000   2000   3000

0   0.4   0.8   1.2   1.6

ELECTRONICS RESEARCH

Los Alamos

Specific Energies of a 10 W System:
Dependence upon Hydrogen Storage Density

Premise:

Stack specific power = 40 W/kg,
(current stack technology)
Regulator, etc. weigh 30 g.

4 wt% H_2 Storage

1.5 wt% H_2 Storage

0.5 wt% H_2 Storage

System Specific Energy (Whr/kg)

System Duration (hr)

Wh/kg v. H2%
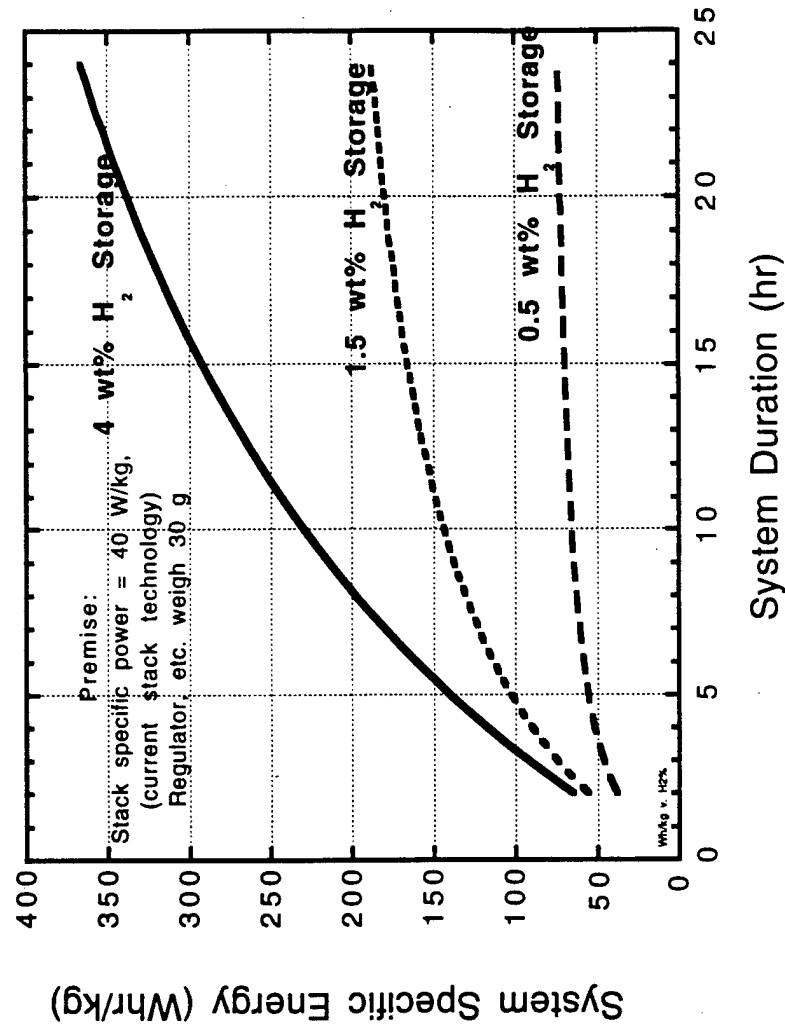
8-CELL STACK PERFORMANCE
on metal hydride cylinder

STACK VOLTAGE (V)

TIME (h)

Current Density
1.0 A/cell
0.75 A/cell

8 Cell Stack,
Gore MEA,
E-TEK Backing,
0.12" FF

Longterm
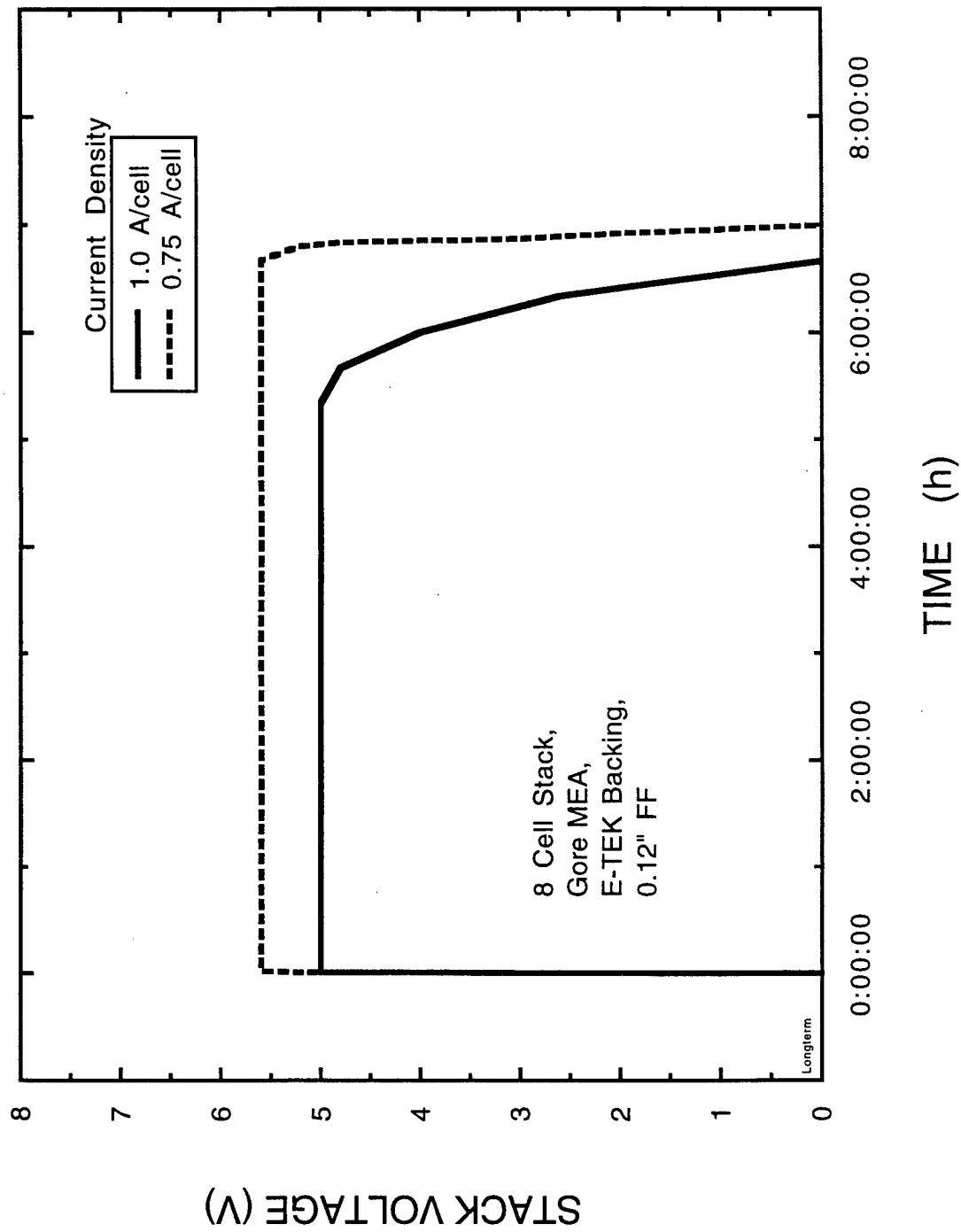
Polymer Electrolyte Fuel Cells at LANL:
Present Status and Future Plans

Two Main Targets of the LANL Core Research Program:

(1) Contribute to demonstration of a power system for transportation based on reformed liquid hydrocarbon fuels and PEFC stack

- R&D efforts to solve critical technology barriers

(2) An ultimate alternative to reformer-based power systems for transportation

- DMFC R&D

ELECTRONICS RESEARCH

Los Alamos
Materials Science and Technology

Polymer Electrolyte Fuel Cells at LANL: Present Status and Future Plans

The Reformate/Air Fuel Cell – Present Status:

● High power density and long-term performance stability demonstrated on neat hydrogen fuel

● The energy conversion efficiency of PEFCs with neat hydrogen feed streams ensures superiority in transportation applications

But,

● Recent concept shift to reformed liquid hydrocarbon fuels adds significant R&D challenges:

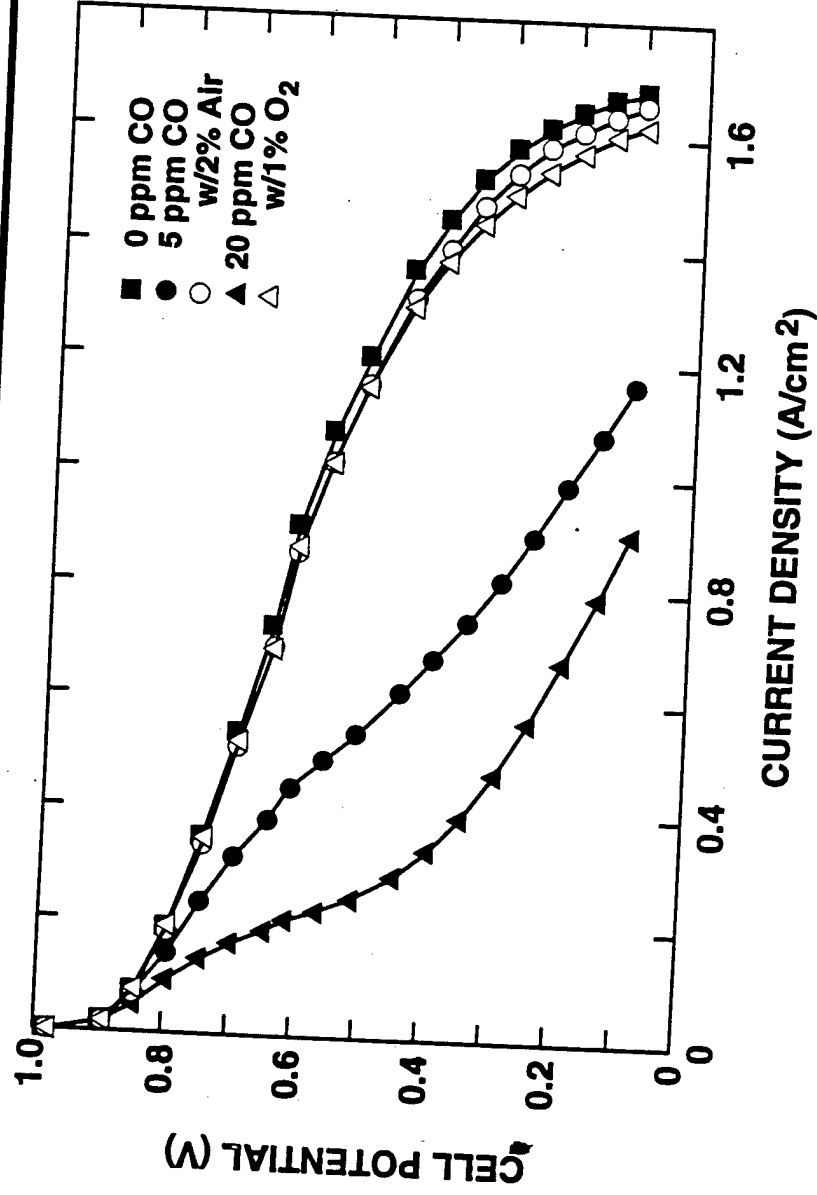Can PEFC advantages for transportation be maintained with liquid hydrocarbon fuels onboard?

ELECTRONICS RESEARCH

Los Alamos
Materials Science and Technology

Polymer Electrolyte Fuel Cells at LANL: Present Status and Future Plans

The Reformate/Air Fuel Cell – Present Status:

● Can PEFC advantages for transportation be maintained with liquid hydrocarbon fuels on-board?

● New R&D issues:

    – Reformer

    – Fuel stream clean-up

    – Stack

    – A remaining target: further cost reduction

CO Effect on Pt Anode
H$_2$/Air = 3/5 atm, 0.14 mg Pt/cm^2 Thin-Film Anode

Legend:
- ■ 0 ppm CO
- ● 5 ppm CO
- ○ w/2% Air
- ▲ 20 ppm CO
- △ w/1% O$_2$

CELL POTENTIAL (V)

CURRENT DENSITY (A/cm^2)

ELECTRONICS RESEARCH

Los Alamos
Materials Science and Technology

Polymer Electrolyte Fuel Cells at LANL: Present Status and Future Plans

Direct Methanol Fuel Cells: The ultimate alternative to reformer-based power systems for transportation

● 1996 DMFC critical targets

– High performance at lower cost with optimized Pt-Ru catalysts

– Demonstrated long-term performance stability

– Significantly lower fuel efficiency loss
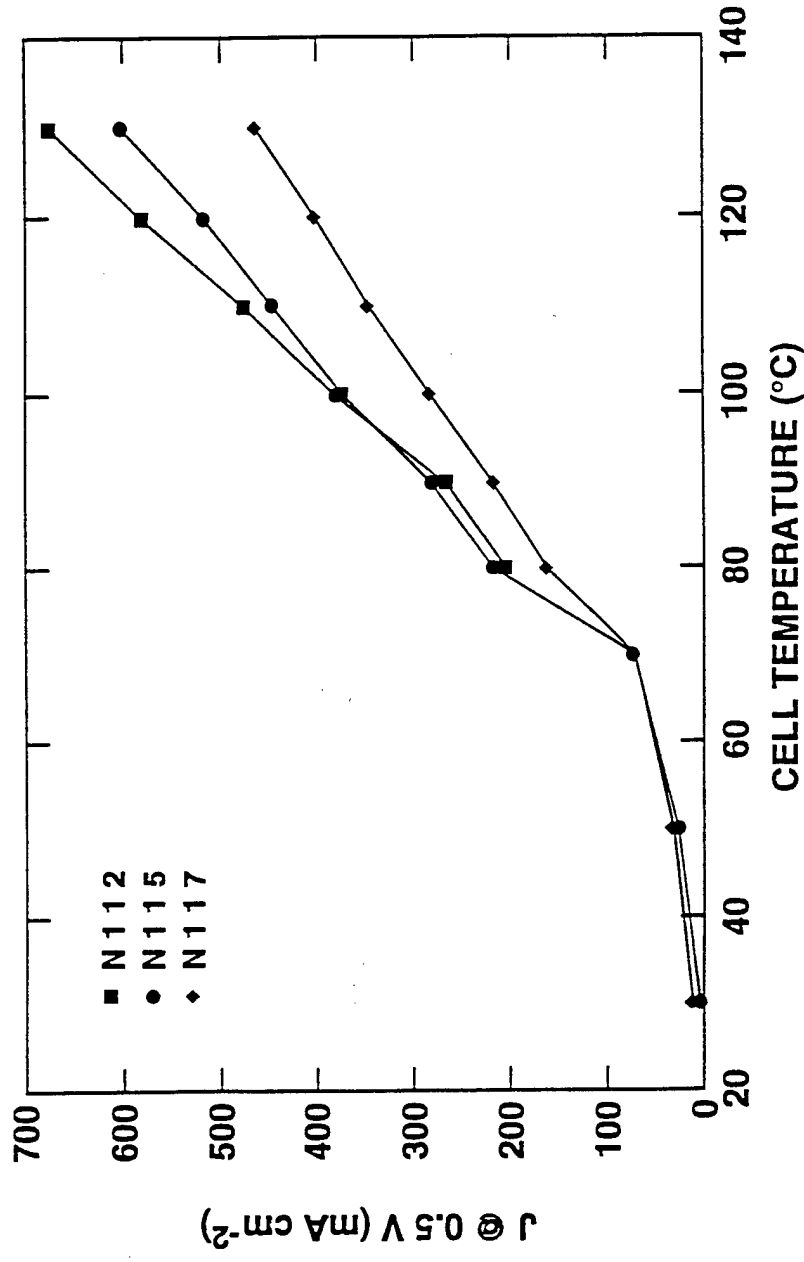
– "Anode Electrocatalyst of the Future"

ELECTRONICS RESEARCH

Los Alamos
Materials Science and Technology

The Direct Methanol Fuel Cells:
Conclusion

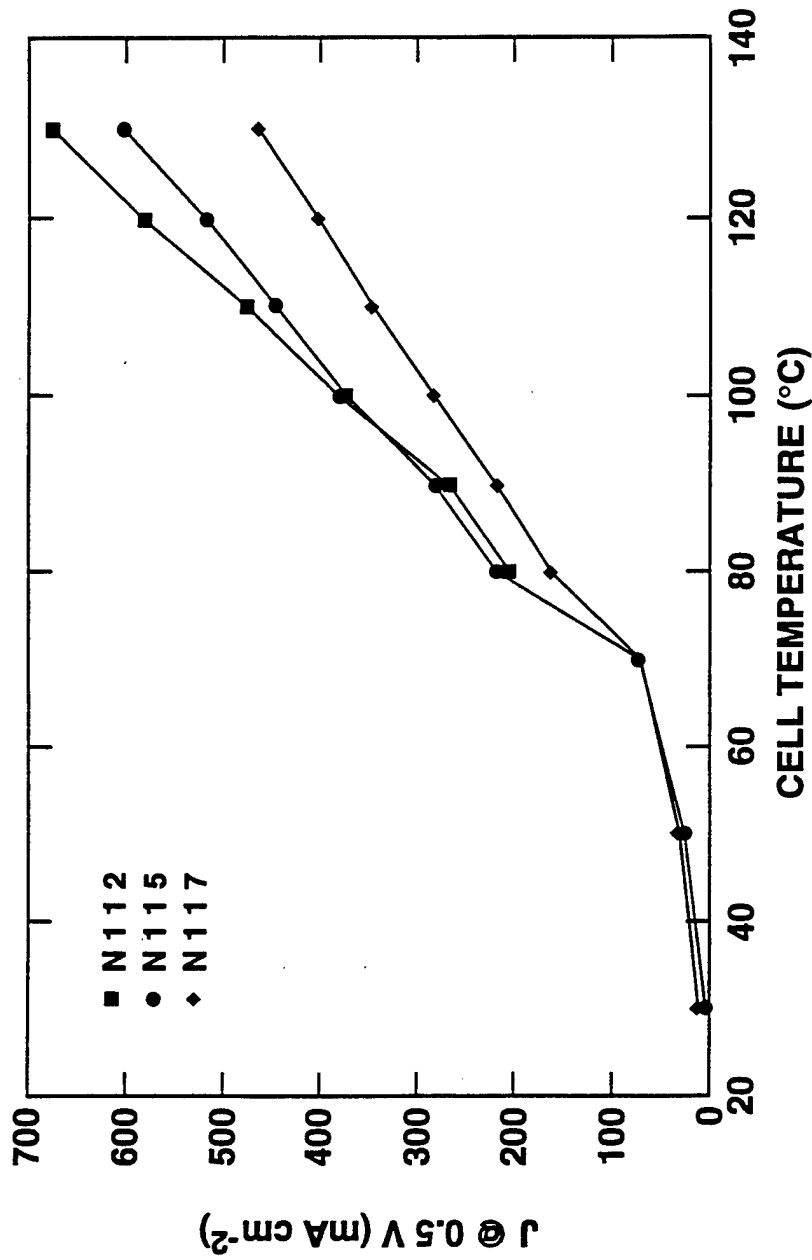*Polymer Electrolyte DMFCs should be aggressively further investigated for transportation applications, based on:*

(1) Recent climb on ascending branch of the learning curve has been aggressive and the present slope of the curve seems to be steep

(2) Simplicity of the overall system may provide an attractive alternative to power systems based on liquid fuel reforming

(3) Performance/efficiency of reformer based systems could probably be matched

(Issues of fuel infrastructure have to be resolved)

ELECTRONICS RESEARCH

Los Alamos
Materials Science and Technology

DMFC Performance:
Temperature and Nafion Membrane Thickness

J @ 0.5 V (mA cm⁻²) — vertical axis, values 0, 100, 200, 300, 400, 500, 600, 700

CELL TEMPERATURE (°C) — horizontal axis, values 20, 40, 60, 80, 100, 120, 140

■ N 1 1 2
● N 1 1 5
♦ N 1 1 7

Los Alamos
Materials Science and Technology

ELECTRONICS RESEARCH

DMFC Performance:
Temperature and Nafion Membrane Thickness

Cell Power for Polymer Electrolyte DMFC
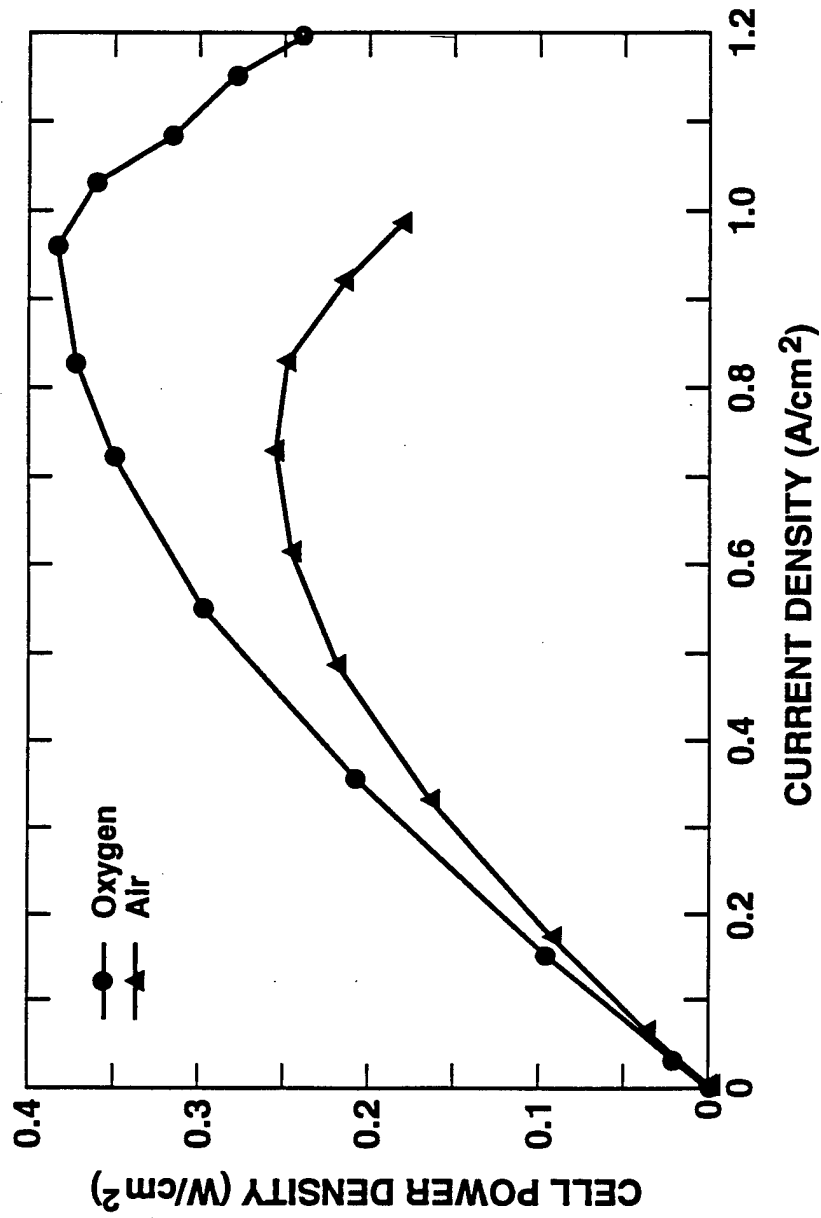
HISTORICAL PERSPECTIVES ON DISPOSABLE FUEL CELLS

Patrick Grimes
Grimes Associates
504 Mountain Avenue
Westfield, NJ 07090-3036

General histories of fuel cells usually start with a mention of the Grove fuel cell, Figure 1. This picture of a <u>regenerative</u> hydrogen oxygen fuel cell system is generally rapidly passed over to proceed to the new modern fuel cells.

Grove in his work on organic fuels operating ethylene fuel cells and carbon monoxide fuel cells. He also worked on chemical hydrides to suppy hydrogen to a hydrogen air fuel cell system. Figure 2 shows 6 cells in series. Grove planted many seeds for fuel cell developments of today.

There are many historical items which bear upon the search of a disposable fuel cell. First, we must define a disposable fuel cell. It ranges from a fuel cell which is disposed in the trash during or after use to fuel cells which dispose of the spent reactants/products (and electrolyte) after use. The fuel cell is then renewed with fresh reactants (and electrolyte).

There are too many references relative to disposable fuel cells to consier all in this brief presentation. We have limited the discussion by choosing some from the early 60s - 30 years ago.

In the early 60s the discussion was mainly on alkaline and acidic, low temperature systems. Fuels included methanol, ethanol, higher alcohols, acetaldehyde, formaldehyde, formic acid, formate, ethylene glycol and higher glycols, as well as sugar, starch, and others. Oxygen/air s well as hydrogen peroxide, chlorite and chlorates, permanganate nitric acid were among the oxidants.

The performance of air electrodes in alkaline electrolyte was found by Kordesch to be dependent upon the type of electrolyte, the hydrogen peroxide formation, oxygen activation catalysts, peroxide decoposition catalysts and the electrode strucurs. While Pt at 1 mg/cm^2 and Ag catalysts gave better performance at low currents, peroxide decomposition catalysts gave better performance at higher currents in alkali, Figure 3. The experimentl electrodes were porous thin hydrophobic nickel plaques, 0.008 in. Thick and coated with catalyzed carbon (0.03 and 0.25 in. thick). They all gave 40-50 mv Tafel slopes on air, Figure 4. The performance on oxygen on the platinum catalyzed electrodes was essentially independent of the thickness of the coating, indicating diffusion limitations with air.

Sodium hydroxide gave better long-term performance than potassium hydroxide at 6 N with Pt on carbon electrodes with CO_2 containing air, Figure 5. The longevity of spinel catalyzed electrodes was on average 5 times greater than Pt on carbon electrodes. The spinel was $CoO*Al_2O_3$, Figure 6. The performance with 6 M KOH with 0.4 M and 1.0 M K_2CO_3 was essentially the same on scrubed air, Figure 7. Electrodes had mechanical damage with time. The greater the degree of "non wetting", repellence, the longer life. NaOH is less wetting than KOH. Pt catalyzed electrode are more wettable. Higher current densities shorten the lives of electrode. Experiments with porous metal electrodes indicate that "wet" or gas pressure balanced electrodes have low tolerance for CO_2, a few hours, and are not reversible. They tend to crack. Thin flexible electrodes could be washed with water and restored to near new performance.

Methanol air fuel cells iwth sulfuric acid electrolyte were studied by K. Williams at Shell and C. Heath ta ESSO (Exxon). Shell made 40 cell systems operating at 300 watts and 12 volts. Esso made similar systems.

The electrodes were made by evaporating gold onthin porous PVC and catalysts then were applied to the metal substrte. The cost was $1.50 ft^2. The inter cell distance was 0.030 in. with an IR loss of 0.045 volt at 100 ma/cm^2. The voltage of the air electrode was depressed by 20-60 mv by methanol, Figure 8. The cell voltage current curves are given in Figure 9. The operating cells had an ester like odor. Ether extracts of the electrolyte showed in addition to the expected formaldehyde and formic acid traces of acetic propionic, butyric, and isobutyric acids. (Ether solvent for the extraction would mask the production of ether in the acidic cells. Later private discussions with Williams said that ethers were found inthe anode exhaust gas.) Injection of these materials into fresh cells showed poisoning of methanol anodes.

Methanol air cell with 10 M KOH and 4.5 M methanol alkaline electrolyte were operated by Vielstich. He used 2-5 mg/cm^2 Pt on porous metal carriers for anodes and porous carbon electrode for cathodes. The cathodes were made hydrophilic with polyethylene in organic solvent. They were 5 to 10 mm thick and 250 cm^2. There was no penetratio of alcoholic electrolyte into the electrodes even after 10,000 hours of operation. The open circuit was 0.9 v with 0,5 amp at 0.75-0.6 volt and 2 amps at 0,6-0,5 volt. The methanol evaporation limited the methanol usage. The evaporation was about 5 mg/hour. The system calculation was 300 Wh/Kg over more than 6000 hours and 1000 amphr/liter, 5-7 kWh/liter.

Vielstich also operated ethylene glycol air cells. In acid the product is CO$_2$ but the potentials are less than formic acid. In alkali the products are oxalate there is a strong dehydrogenation at 60-90 and currents of 600 ma/cm^2 can be obtained. Porous nickel was used for the anodes either as a double skeleton coin or as a flame sprayed Raney nickel on porous nickel.

Formic acid fuel cells have better performance in acid on Pt catalyzed electrodes than methanol and formaldehyde. There is a poisoning effect with time. Frumpkin found tht Pt/Ru reduced poisoning and allowed a 3-fold improvement. However, in both cases the current yield was about 20% with corresponding decomposition of formic acid.

Formate is the initial primary product in the oxidation of methanol in alkali with platinum. The further oxidation occurs at a lower potential. Grimes and Spengler observed that there is complete oxidization of methanol to carbonate ion with Pt/Pd mixed catalyst. Formate cells can have an order of magnitude greater power than methanol cells.

Alloy catalysts were reported by Vielstich for the oxidation of formate. He found in scans that a peak current density was observed with Pd/Ag and Pd/Rh, Figure 11.

Alloys for the oxidation of methanol were studied extensively by Binder et al. They made Raney catalysts on gold skeletons using leachable sodium chloride for macropores. The map of alloys is shown in Figure 12. Here is significant effects with the alloys both in acid and in base, Figure 13-19. Binder postulates that the catalytic activity correlates to the magnetic susceptibility of the alloys, Figure 20.

Grimes and Spengler have operated formate ion fuel cells with KOH and K$_2$CO$_3$ electrolytes with good performance. The studied the effects of Pt/Pd ratio and found that the lower ratios were most effective, Figure 21 and Figure 22. The output of formate ion cells approaches that of hydrogen and hydrazine oxygen cells.

Fuel cells with hydrogen peroxide as an oxidant were developed at Allis Chalmers by Grimes et al. Mixed electrolyte solutions of fuel, alcohol, and oxidant - hydrogen peroxide - in electrolytes of hydroxide, carbonate and bicarbonate ions. Specific activity of catalysts were used

to direct the action of anodes and cathodes in separatorless cells. Pt on nickel surfaces were used for anodes, and silver on nickel were used for cathodes. This allowed simple bipolar construction and single pump design. A 40-cell system with 100 cm^2 electrodes was built. Outputs of 15 volts and 400 ma/cm^2 amps at ambient temperatures were obtained. Adaptation of alloy catalysts would markedly improve performance, Figure 24. A smaller scale version were sold as demonstration kits for students and others Figure 25 and 26.

Many investigators inthe past have done significant work which will aid the developers of disposable fuel cells for the future. Read the literature.
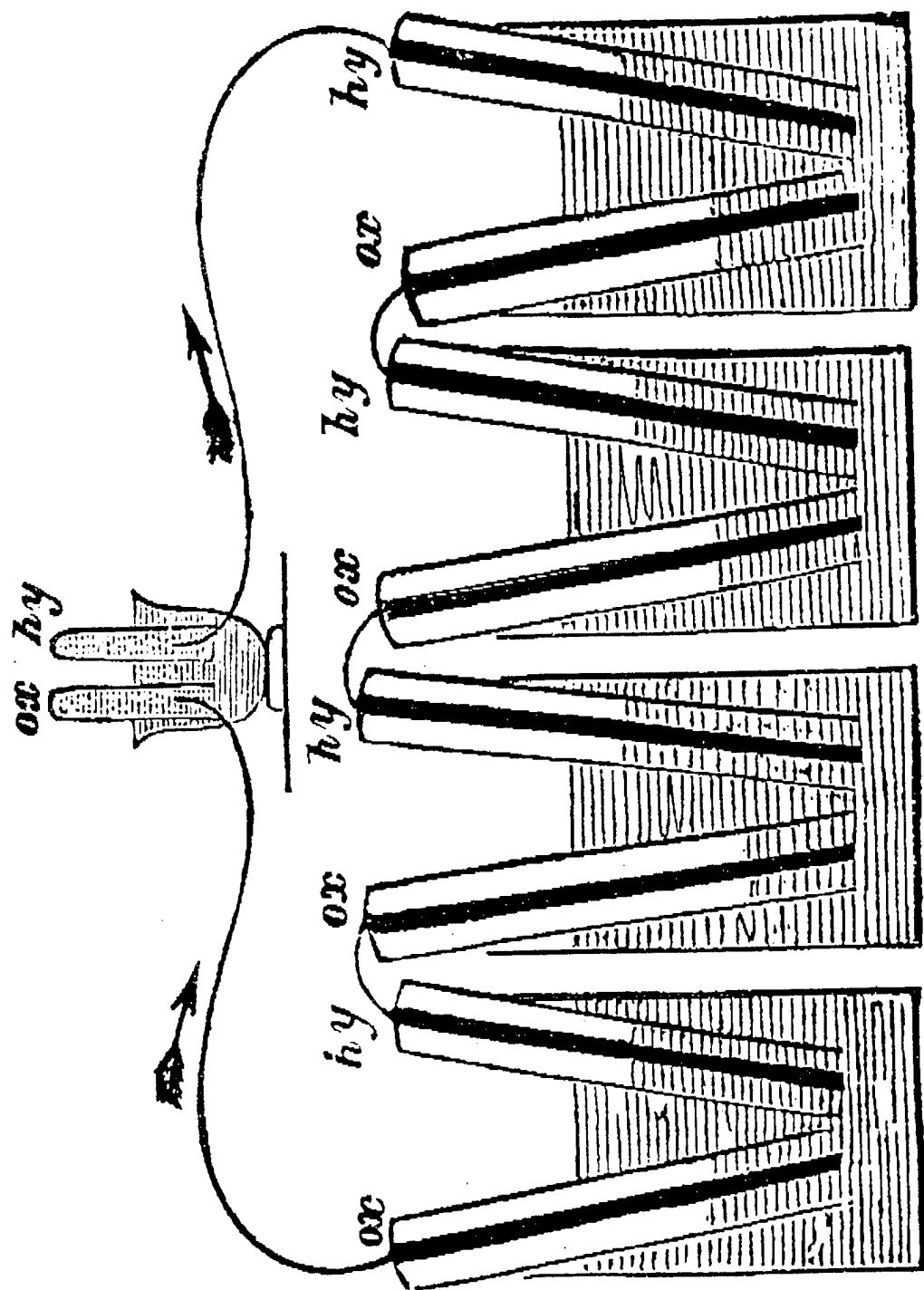
Fig. 1 Four cells of Grove's H_2/O_2 battery [3], here used to drive an electrolysis cell "to effect the decomposition of water by means of its compusition."
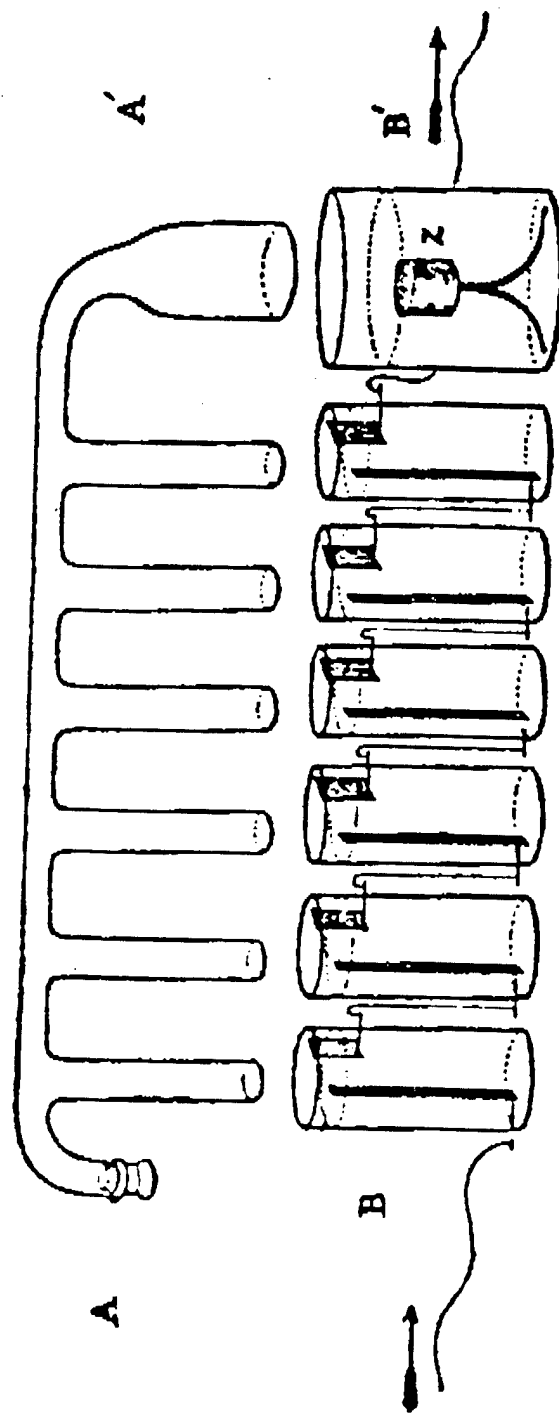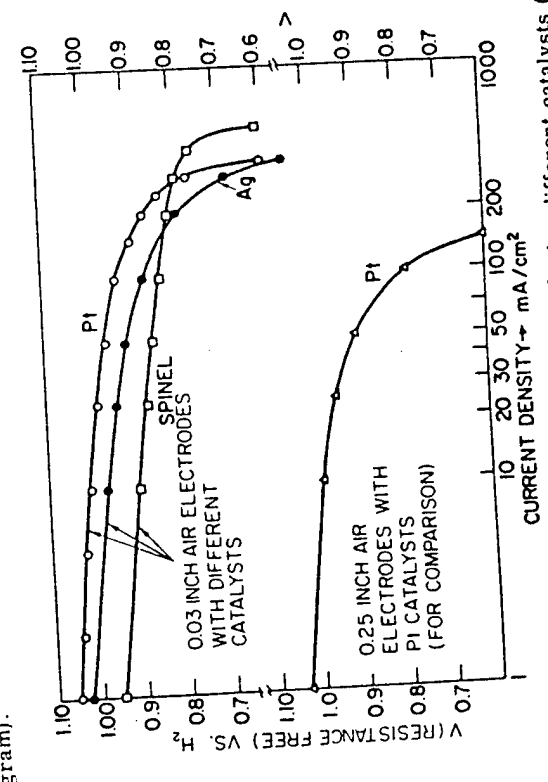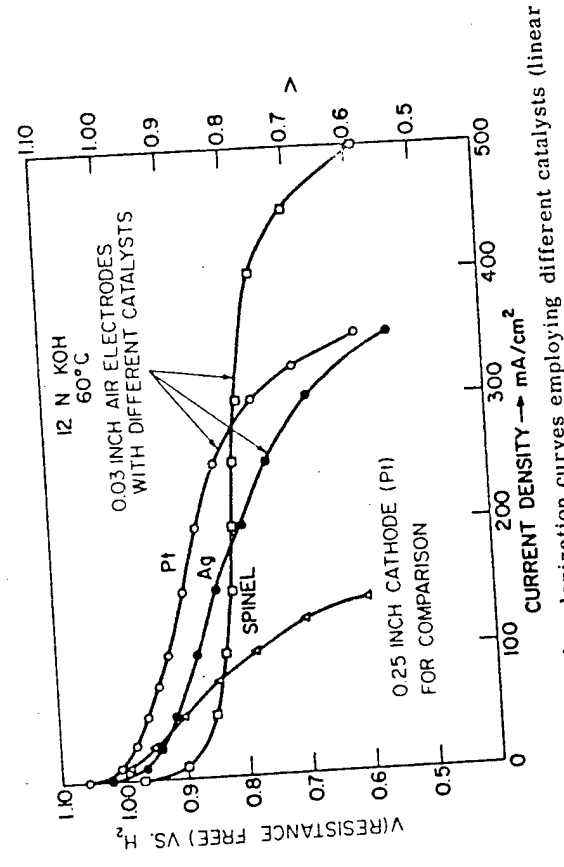
Fig. 2.2-2 Grove's H_2/air battery with zinc hydrogen-generator [3]. The zinc (Z) generates hydrogen that reaches the anodes through the manifold when it is lowered.

Fig. 5 Operational life of Union Carbide fixed-zone air electrodes (1965).

Fig. 6 Performance with CO_2-containing air, comparing noble metal-cata-ad vs. spinel-catalyzed cathodes.

Fig. 7 Performance with CO_2-containing air, comparing platinum-catalyzed cathodes 6 N KOH vs. 6 N NaOH.

Fig. 3 Electrode polarization curves employing different catalysts (linear diagram).

Fig. 4 Electrode polarization curves employing different catalysts (logar-unmic diagram).

Fig. 8 Polarization curves for oxygen and air electrodes in sulfuric acid solution at 25°C.
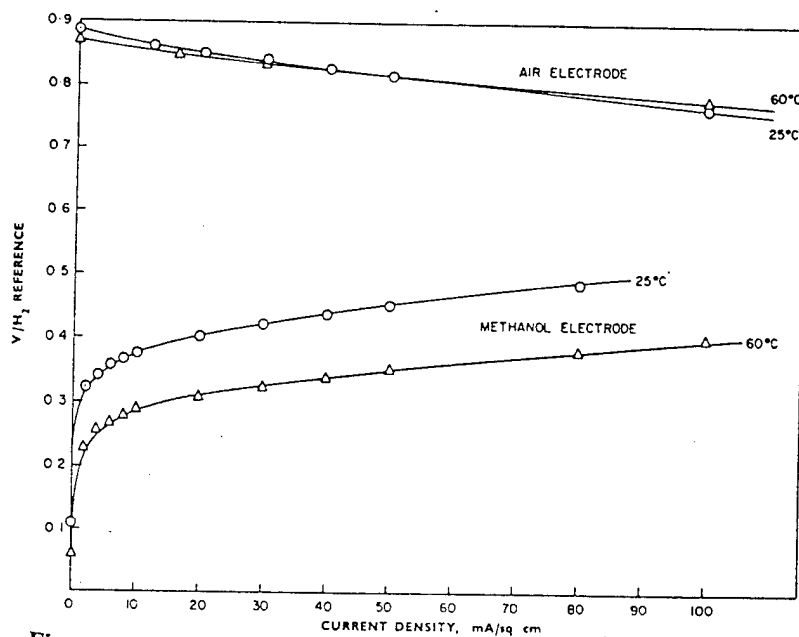
Fig. 9 Polarization curves for air and methanol electrodes in a 1 M CH$_3$OH−6 N H$_2$SO$_4$ mixture at 25° and 60°C.

ALCOHOL–AIR FUEL CELLS
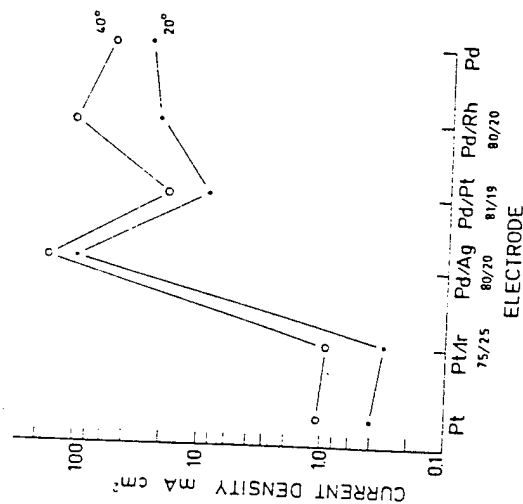
Fig. 11 Peak current density of a triangular potential scan from Fig. 5 on different smooth metal electrodes in 6 N KOH + 4 M HCOOK.
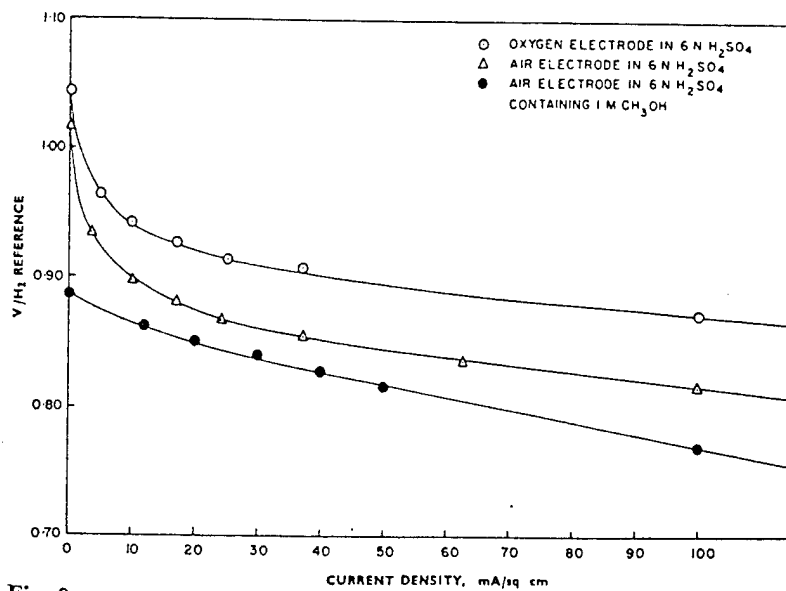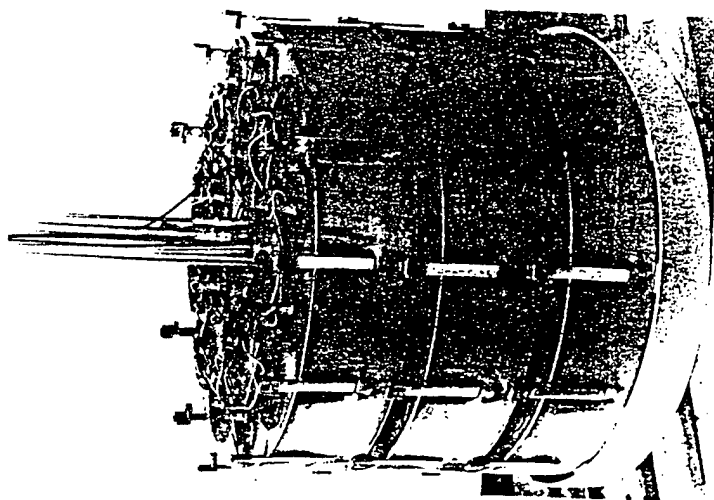

Fig. 8. Three cells of a 10-cell, 60-W methanol-air battery with cylindrical air diffusion electrodes for a flashing sea buoy (courtesy of Brown, Boveri and Cie., Baden, Schweiz).
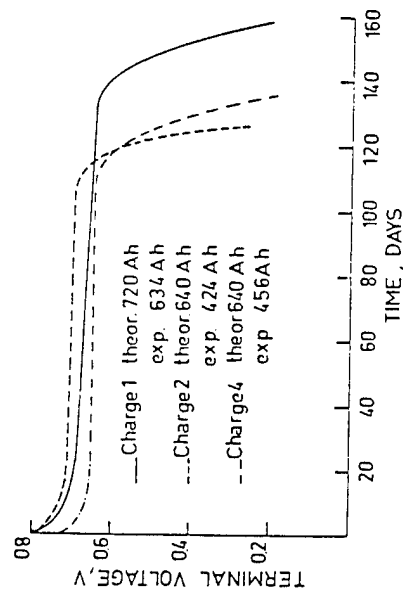
Fig. 10 Terminal voltage at periodic loads (2 sec load and 4 sec open circuit) of a methanol-air cell, operating time τ > 12,000 hours with 4 electrolyte charges, temperature 10°–20°C.

Fig. 12

Potentials with Alloy Catalysts[a]

|	Ru	Rh	Pd	Os	Ir	Pt	Au
Ru	350/≥900						
Rh	300/500	420/540					
Pd	290/490	520/580	570/800				
Os	290/≥900	320/540	340/720	320/880			
Ir	300/440	380/520	400/580	350/500	350/560		
Pt	230/400	330/510	480/610	250/440	290/490	370/540	
Au	310/≥900	460/580	650/780	400/≥900	300/540	380/580	≥900/≥900

[a] Fifty atom % with $2\,M$ methanol in $4.5\,N$ H_2SO_4 at 25°C (lower figures) and 80°C (upper figures); current density: $50\ mA/cm^2$.

Fig. 20 . Magnetic susceptibility of alloys of Pt metals as a function of composition (data from the literature).

Fig. 16 Potential-current density plots of electrodes containing Raney Pt metals with CH₃OH in 4.5 N H₂SO₄ at 80°C.

potential - mV

current density - mA/cm²

2 M CH₃OH
4.5 N H₂SO₄, 80°C

Pd
Ru
Pt
Rh
Ir
Os
Au

Fig. 17 Potential-current density plots of electrodes containing Raney Pd alloys with CH₃OH in 4.5 N H₂SO₄ at 80°C.

potential - mV

current density - mA/cm²

2 M CH₃OH
4.5 N H₂SO₄, 80°C

Pd Rh
Pd Pt
Pd Ir
Pd Os
Pd Ru

Fig. 18 . Potential-current density plots of electrodes containing Raney Pd alloys with CH₃OH in 4.5 N H₂SO₄ at 25°C.

potential - mV

current density - mA/cm²

2 M CH₃OH
4.5 N H₂SO₄, 25°C

Pd Pt
Pd Ru
Pd Ir, Pd Rh
Pd Os
Pd Ru
Pd

Fig. 13 Potential-current density plots of electrodes containing Raney Pt metals with CH₃OH in 5 N KOH at 25°C.

potential - mV

current density - mA/cm²

2 M CH₃OH
5 N KOH, 25°C

Pd
Pt
Ir
Rh
Os
Ru
Au
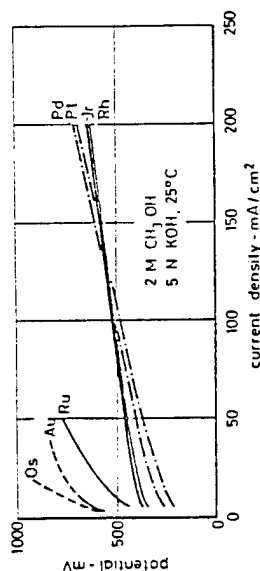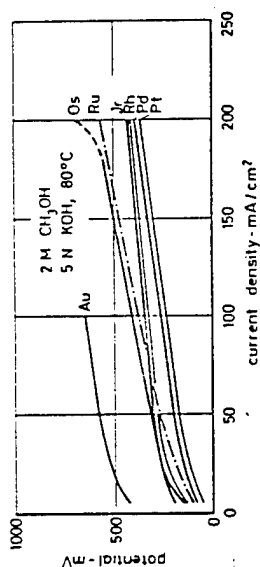
Fig. 14 Potential-current density plots of electrodes containing Raney Pt metals with CH₃OH in 5 N KOH at 80°C.

potential - mV

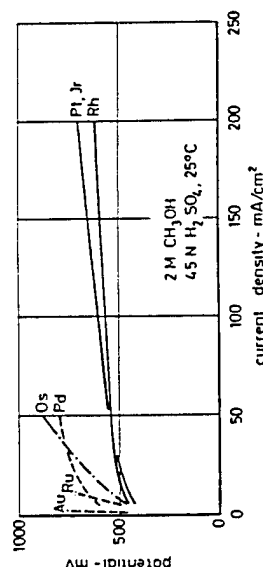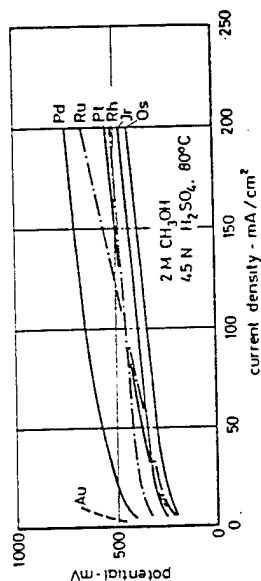current density - mA/cm²

2 M CH₃OH
5 N KOH, 80°C

Os
Ru
Ir
Rh
Pd
Pt
Au

Fig. 15 Potential-current density plots of electrodes containing Raney Pt metals with CH₃OH in 4.5 N H₂SO₄ at 25°C.

potential - mV

current density - mA/cm²

2 M CH₃OH
4.5 N H₂SO₄, 25°C

Pt, Ir
Rh
Os
Pd
Au, Ru

ANODE 60 Pd – 0 Pt

CATHODE 30 Pd – 30 Pt

• TEMP 30°C
○ TEMP 90°C

HALF–CELL VOLTAGE VS. SCE

CURRENT DENSITY (ASF)

Fig. 22 Halfcell voltages for the better anode and cathode combined in a single cell with 4 M potassium formate and 4 M potassium hydroxide.

• 60 Pd – 0 Pt Mg/IN²
○ 50 Pd – 10 Pt Mg/IN²
□ 40 Pd – 20 Pt Mg/IN²
◁ 30 Pd – 30 Pt Mg/IN²
▽ 0 Pd – 60 Pt Mg/IN²

CATHODE VOLTAGE VS. SCE
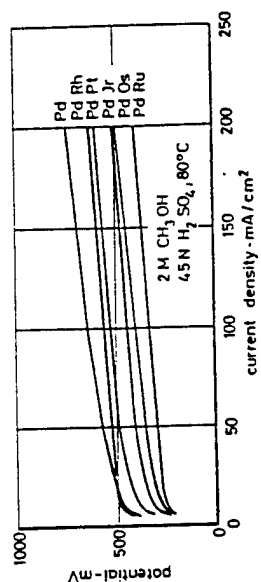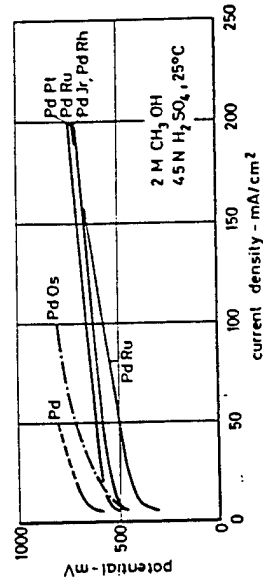
CURRENT DENSITY (ASF)

Fig. 21 Effect of catalyst on cathode potentials in 4M KCOOH and 4 M KOH at 90°C.

Fig. 26   Fuel Cell Demonstration Unit.
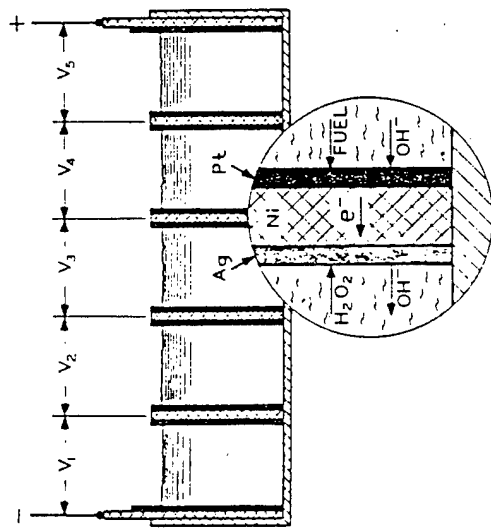
Fig. 25   Bipolar Fuel Cell.
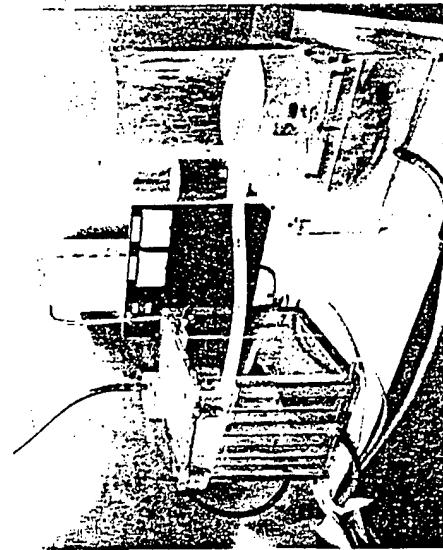
Fig. 24 | Experimental Methanol-Hydrogen Peroxide Fuel Cell.

DISPOSABLE FUEL CELLS AND LIFETIMES

Anthony B. LaConti
Giner, Inc., 4 Spring St.
Waltham, MA 02154-4497

A study has been initiated on possible low-cost and stable materials that could be used in "disposable fuel cells" that operate for 10's of hours to 500 hours. The shorter mission times may allow use of materials tha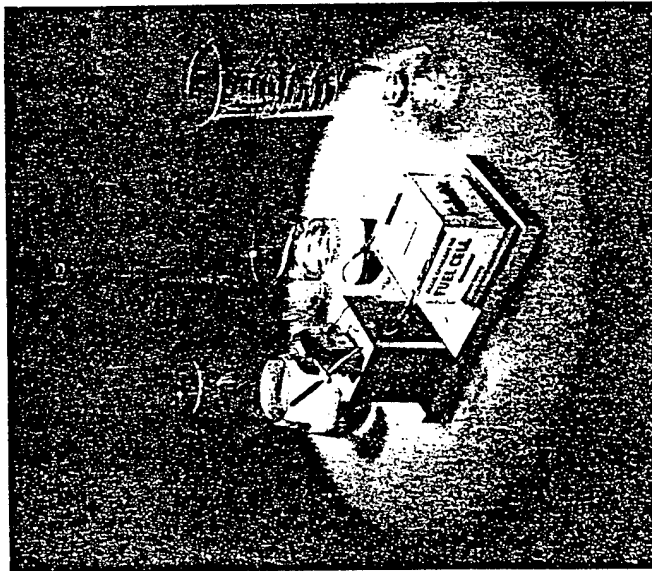t have not been seriously considered for long-life proton-exchange membrane fuel cell (PEMFC) applications (4,000 to 50,000 hours).

Hydrogen/air as well as direct methanol/air PEMFC are being actively developed as replacement for high-energy-density military batteries in ARPA-sponsored programs. Some candidate low-cost membrane, catalyst and hardware materials for these applications will be reviewed.

The useful life of PEMFC is dependent on 1) ionomer membrane, 2) electrode structure and support, 3) hardware materials/design, and 4) operating conditions. A limited number of proton-exchange membrane sites and catalyst sites are available, thus contamination from the materials or fillers used near the membrane and electrode assemblies (MEAs) must be avoided. The effect of certain ions on MEA contamination is shown in Figure 1. Also PEMFCs operating with H_2 and O_2 (air) have been found to degrade through a peroxyl mechanism, resulting from the permeation of the O_2 through the membrane to the PEM/H_2 catalyst interface where peroxyl species form and tend to degrade the membrane (LaConti et al., 1977, 1982, 1988; Scherer, 1990). The postulated MEA degradation mechanism is shown in Figure 2.

Factors that tend to accelerate membrane degradation and early life PEMFC failures include: 1) ionic contamination ($Fe^{++} >> Cu^{++} > Ni^{++} > Na^+$), 2) increasing temperature, 3) peroxide formation (increased O_2, H_2 permeability and dry operation (indirectly, higher peroxide concentration). The effect of these accelerants on membrane degradation is depicted in Figures 3 and 4. The expected life for select membranes in an accelerated medium and in a cell is shown in Figures 5 and 6, respectively.

For liquid feed direct methanol PEMFC (DMPEMFC) many of the factors leading to membrane degradation listed above are absent, making use of certain low-cost materials attractive. The performance-life curve for a 50-watt DMPEMFC stack is shown in Figure 7. Ultimately the catalyst loading for DMPEMFC must be reduced close to the levels being considered for H_2/air PEMFC (Wilson and Gottesfeld, 1992).

The PEMFC requires the use of inexpensive, as well as lighter weight constructional materials if it is to be used extensively for battery replacement applications. For example, the cost of the highly stable fluorocarbon sulfonic acid membranes being developed by DuPont, Gore, Dow (Possible Sale of the Business), Asahi Glass (Japan). Asahi Chemical (Japan) and Chlorine Engineering Corp. (Japan), and Ballard (Canada) may have to be decreased significantly for wide-use battery replacement applications.

For H_2/air or direct methanol/air PEMFC some of the possible material candidates (Figure 8) for typical military battery missions up to 500 hours include:

1. <u>Membranes</u>: sulfonated-polystyrene grafts (RAIPORE Product Guide), styrene-ethylene/butylene styrene (Wnek et al., 1995), double-crosslinked FEP-g-polystyrene

membranes, (Büchi et al., 1994), poly 2.6-diphenyl 1,-4 phenylene oxide) (Hogdon and Hay, 1970), poly(aryl ether sulfone) (Nolte et al., 1993a; 1993b), poly (aryl ether ketone) (Helmer-Metzman et al., 1993), and a series of organic/inorganic polymers (Gautier-Luneau et al., 1992) an inorganic polymers (Lundsgaard et al., 1992).

2. <u>Catalysts</u>: supported-Pt catalyst (Wilson and Gottesfeld, 1992); supported Pt-Ru/WO_3 (Chen et al., 1995); supported Pt-Ru (Kosek et al., 1995a).
3. <u>Collectors/Flow Fields</u>: molded carbons (Lawrence, 1980) molded TiC (Kosek, 1994), injected molded polypropylene-graphite (Exxon, Alsthom), conductive plastics, and coated stainless and coated Ti.
4. <u>Plastic Frames/Gaskets/Enclosures</u>: polysulfone, Lexan, Kynar, EPDM (EPR), polypropylene.

The potential extension of the PEMFC to alkaline systems has been studied (Swette et al., 1993). The potentially attractive feature for an alkaline fuel cell is the greater selection of low-cost materials of construction available. For example, the materials cost for the Alsthom circulating alkaline electrolyte system is estimated at $10/kW (Appelby, 1995). A major limitation for an alkaline membrane fuel cell is 1) susceptible to CO_2 contamination, 2) relatively poor ionic conductivity, and 3) the instability of anion-exchange membranes versus the PEMs. Recently very promising results have been reported for aqueous carbonate form are more stable than the corresponding hydroxide ion membranes; however, to achieve some reasonable conductivity and performance, operating temperature would have to be near 10°C. A dissolved methanol alkaline/carbonate fuel cell may be attractive for some low-power, short missions. Non-noble air cathode structures of silver or macrocyclics on carbon should not parasitically react, and can tolerate the dissolved methanol. Anodes comprised of Pt/Pd are very efficient for direct methanol oxidation in alkaline media. For alkaline fuel cells some of the possible material candidates (Figure 9) for short (200 hours or less), low power missions include:

1. Quarternary Ammonium (QA) Membranes (PSQA Grafts (RAIPORE Product Guide), Aliphatic QA (LaConti, 1967), Fluorinated QA (Matsui et al., 1986, 1987a, 1987b))
2. Catalyst (Raney Ni, Ag, Co, and Fe Macrocyclic, Pyochlores, Pt/Pd)
3. Collectors (Ni/Alloys, Steels, injected molded polypropylene carbon)
4. Frames/Gaskets (Polypropylene, EPDM)

Some of the alternative energetic <u>air</u> electrode battery couples that have been studied in the past and may be of possible interest for review include: N_2H_4/O_2; OH-, NH_3/O_2; OH- (Austin, 1971), Zn/O_2; OH- (Bayles and Saunders, 1995), Al/O_2; OH- (Rudd and Gibbons, 1994), BH_4/O_2; OH- (Bard et al., 1985) and LiO_2; OH- (Littauer and Tsai, 1978). Most of the anode couples listed above are highly energetic and can also be used to electrochemically generate H_2 from H_2O and yield high energy densities. For example, the Al/H_2; OH- and Li/H_2; OH- couples can yield voltages of 0.6-0.7 V and 1.4-1.5 V, respectively, at reasonable current densities (100 mA/cm^2 or greater). Air is not required, thus CO_2 contamination becomes less of a concern. Management of the byproducts and parasitic losses at the anode are concerns with these couples. The projected performance of some alternative alkaline couples is shown in Figure 10. Comparative PEMFC performance is shown in Figure 1.

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Giner, Inc.

CALCULATION OF AVAILABLE MILLIEQUIVALENTS OF PERFLUOROCARBON SULFONIC ACID FOR NAFION® 115 MEMBRANE

PEM Wet Thickness (mils)   6-7

Initial Ion-Exchange Capacity (meq/cm^2)   0.025

Available meq per 620 cm^2 (48 W) Cell   15.6

Ionic Contamination (meq) to Decrease meq   3.2
of Cell by 20% (lowers performance significantly)

Grams of Select Contaminants – 3.2 meq

Na^+ ion	0.074
Ca^{++} ion	0.064
Fe^{+++} ion	0.038
Al^{+++} ion	0.028

Figure 1.   Effect of Certain Ions on MEA Contamination

Giner, Inc.
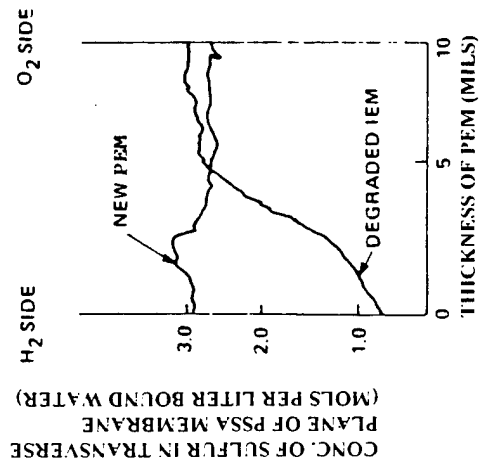
Scanning Electron Microprobe of Polystyrene Sulfonic Acid (PSSA) Membranes from Electrochemical Cells

DEGRADATION MECHANISM

$$Pt$$

STEP 1: $H_2 \rightarrow 2H\cdot$

STEP 2: $H\cdot + O_2$ (Diffused through PEM) $\rightarrow HO_2\cdot$

STEP 3: $HO_2\cdot + H\cdot \rightarrow H_2O_2$ (ℓ) (which can diffuse into PEM)

STEP 4: $H_2O_2 + M^{+2}$ (Fe^{++} & Cu^{++} always found in PEMs) $\rightarrow H^+M^{+3} + H_2O + \cdot OH$

STEP 5: $\cdot OH + H_2O_2 \rightarrow H_2O + HO_2\cdot$ (Attacks PEM)

Figure 2. Postulated MEA Degradation

Giner, Inc.

- IONIC CONTAMINANTS (Fe^{++} >> Cu^{++} > Ni^{++} > Na^+)

- TEMPERATURE

- PEROXIDE FORMATION (H_2, O_2 PERMEABILITY)

- DRY OPERATION (INDIRECTLY)

Figure 3. Membrane Degradation Accelerants

Giner, Inc.
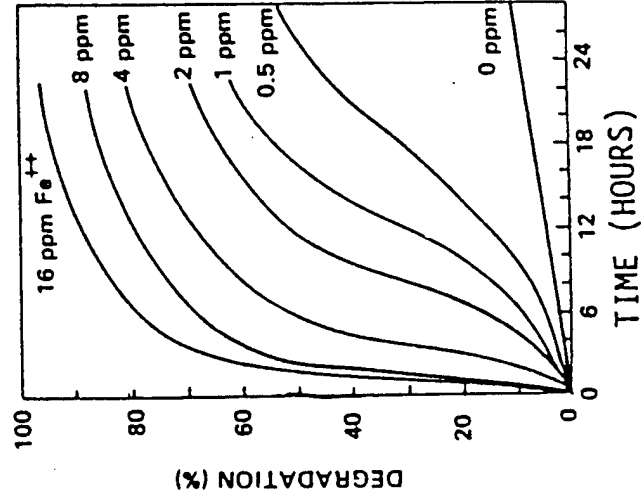
Figure 4. The Accelerating Effect of Ferrous Ion on the Rate of Degradation of Styrene (1% DVB) Membrane in 3% H_2O_2 at 68°C

Giner, Inc.
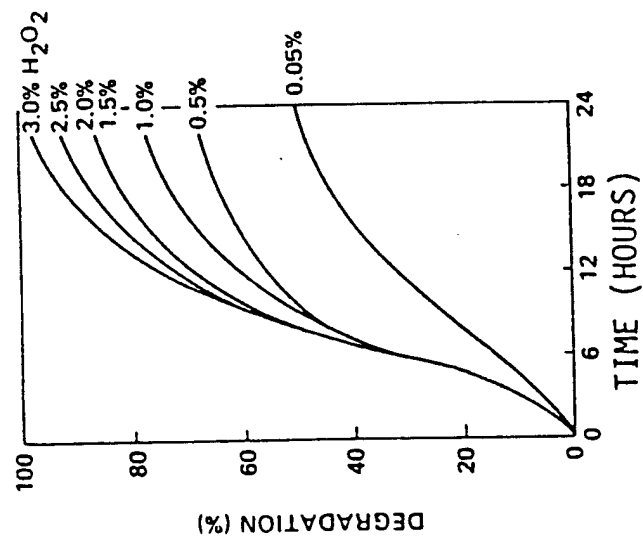
Figure 4. (Cont.) The Accelerating Effect of Hydrogen Peroxide on the Rate of Degradation of
Styrene (1% DVB) Membrane in 4 PPM Fe^{++}, 68°C
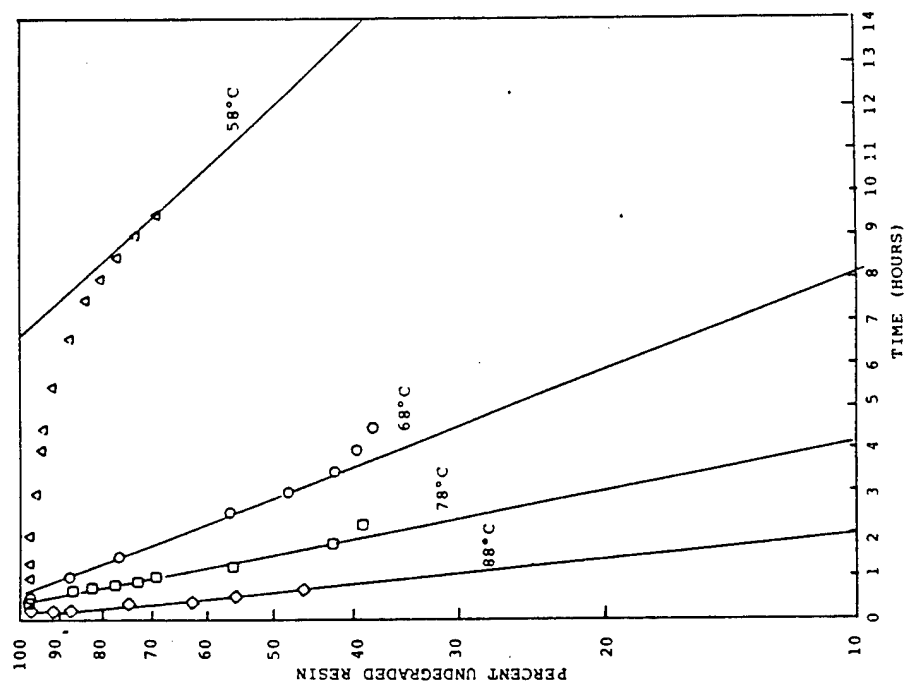
Giner, Inc.

Figure 4. (Cont.) The Accelerating Effect of Temperature on the Rate of Degradation of Styrene (1% DVB) Membrane in 3% H_2O_2, 4 PPM Fe^{++}

Giner, Inc.

3 g MEMBRANES
4.0 PPM FE^{++} in
50ml of 3% H$_2$O$_2$
TEMP. = 68°C

6% DVB CROSSLINKED POLYSTYRENE SULFONIC ACID
OR POLYPHENYLENE OXIDE (P$_3$O) OR POLY (ARYL ETHER
SULFONE) TYPE SULFONIC ACID MEMBRANE

POLYTRIFLUOROSTYRENE OR
POLYVINYLIDINE SULFONIC ACID

NAFION - 120 SULFONIC ACID
MEMBRANES (30% H$_2$O$_2$ - 20 ppm Fe)

1% DVB CROSSLINKED
POLYSTYRENE SULFONIC
ACID

DEGRADATION (%)

100 90 80 70 60 50 40 30 20 10

TIME (HOURS)

0 4 8 12 16 20 24 28

Figure 5. Degradation Rate of Certain Sulfonic Acid Membranes in H$_2$O$_2$/Fe^{++} Media

Giner, Inc.
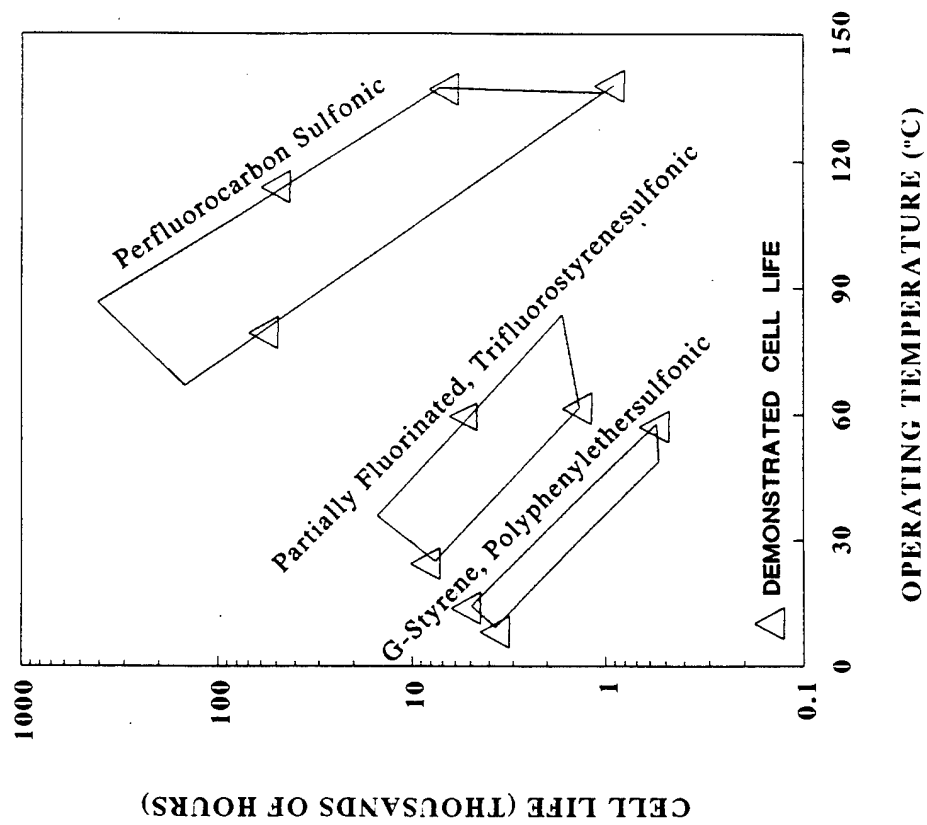
Figure 6. PEM Cell Life Capability

Giner, Inc.
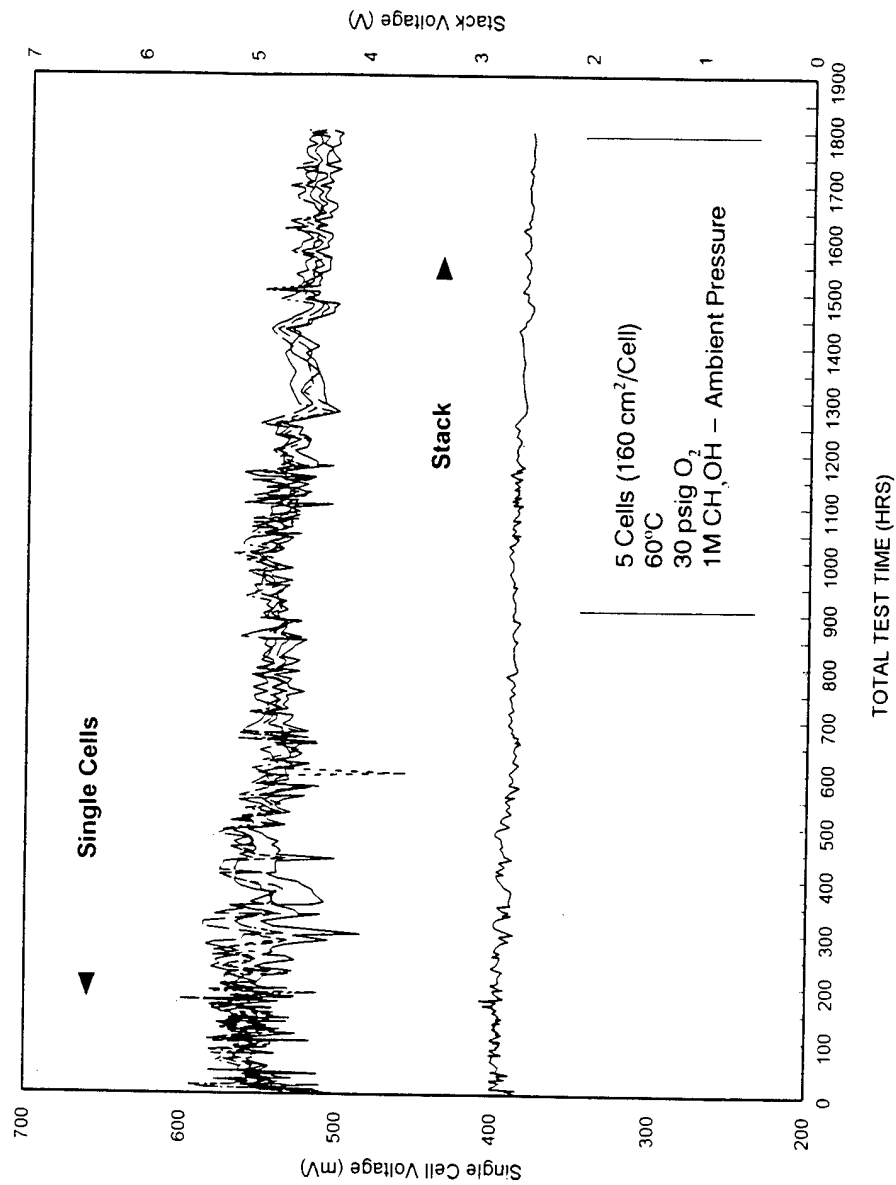
Figure 7. Life Plot of Giner, Inc. 50-Watt DMPEMFC Stack

Giner, Inc.

Membranes:
- sulfonated-polystyrene grafts
- styrene-ethylene/butylene styrene
- double-crosslinked FEP-g-polystyrene membranes
- poly (2,6-diphenyl 1,-4 phenylene oxide)
- poly (aryl ether sulfone)
- poly (aryl ether ketone)

Catalysts:
- Supported-Pt catalyst, Pt-Ru/WO$_3$, Pt-Ru

Collectors/Flow Fields:
- molded carbons or TiC
- injected molded polypropylene-graphite, conductive plastics
- coated stainless and coated Ti

Plastic Frames/Gaskets/Enclosures:
- polysulfone, Lexan, Kynar, EPDM (EPR), polypropylene

Figure 8. Low-Cost H$_2$/Air or Direct Methanol/Air PEMFC Material Candidates for Typical Military Battery Missions up to 500 Hours

Giner, Inc.

- Quaternary Ammonium (QA) Membranes (PSQA Grafts, Aliphatic QA, Fluorinated QA)

- Catalyst (Raney Ni, Ag, Co and Fe Macrocyclics, Pyrochlores, Pd)

- Collectors (Ni/Alloys, Steels, injected molded polypropylene carbon)

- Frames/Gaskets (Polypropylene, EPDM)

Figure 9. Low-Cost Alkaline Media. Alkaline Membrane Fuel Cell Material Candidates for Short (200 hours or less), Low-Power Military Battery Missions

Giner, Inc.

Lithium/H$_2$; Aqueous Electrolyte/Passive
Cathode Battery System

o ANODIC POLARIZATION (LITHIUM ANODE)
• CATHODIC POLARIZATION (NICKEL SCREEN CATHODE)
Δ CELL POLARIZATION

Anode: Li → Li$^+$(aq) + e   V° = -3.05 V
Cathode: H$_2$O(aq) + e → OH$^-$(aq) + ½H$_2$ V° = -0.83 V
Cell: Li + H$_2$O(aq) → Li$^+$(aq) + OH$^-$(aq) + ½H$_2$ E° = 2.22 V
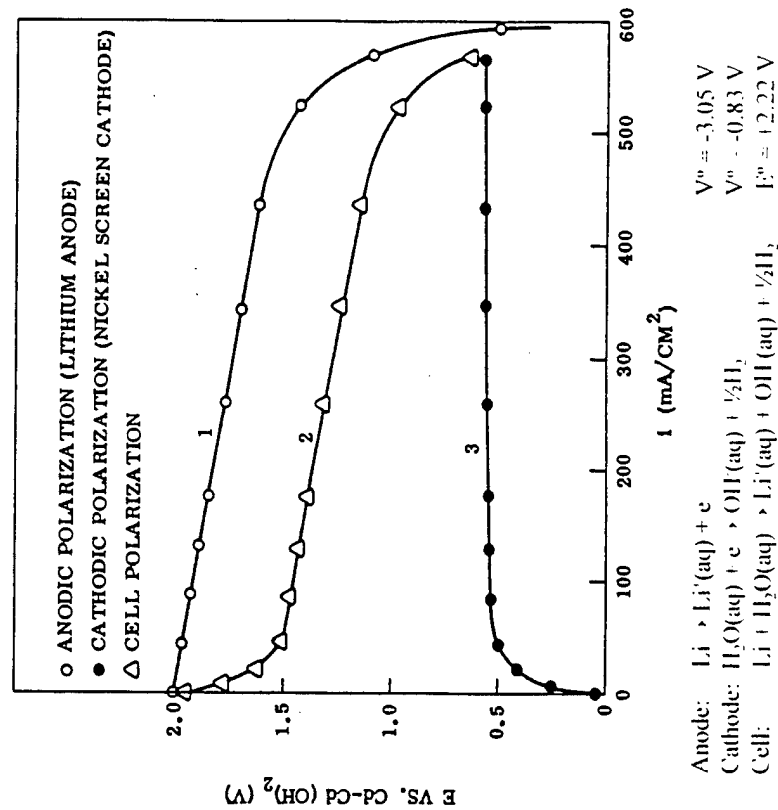
Couple	Calculated OCV Voltage (V)	Estimated Voltage (V) @ 100 ASF*
Li/O$_2$; OH$^-$	3.45	2.3
Al/O$_2$; OH$^-$	2.75	1.3-1.4
BH$_4$/O$_2$; OH$^-$	1.64	---
Zn/O$_2$; OH$^-$	1.62	1.1-1.2
N$_2$H$_4$/O$_2$; OH$^-$	1.42	1.0
H$_2$/O$_2$; OH$^-$	1.23	0.9
Li/H$_2$; OH$^-$	2.22	1.5
Al/H$_2$; OH$^-$	1.52	0.6

*Near ambient

Figure 10. Alternative Alkaline Fuel/Air (O$_2$) or Fuel/H$_2$ Couples

Giner, Inc.

Membrane Comparison
Std Pt Black Anode & Cathode
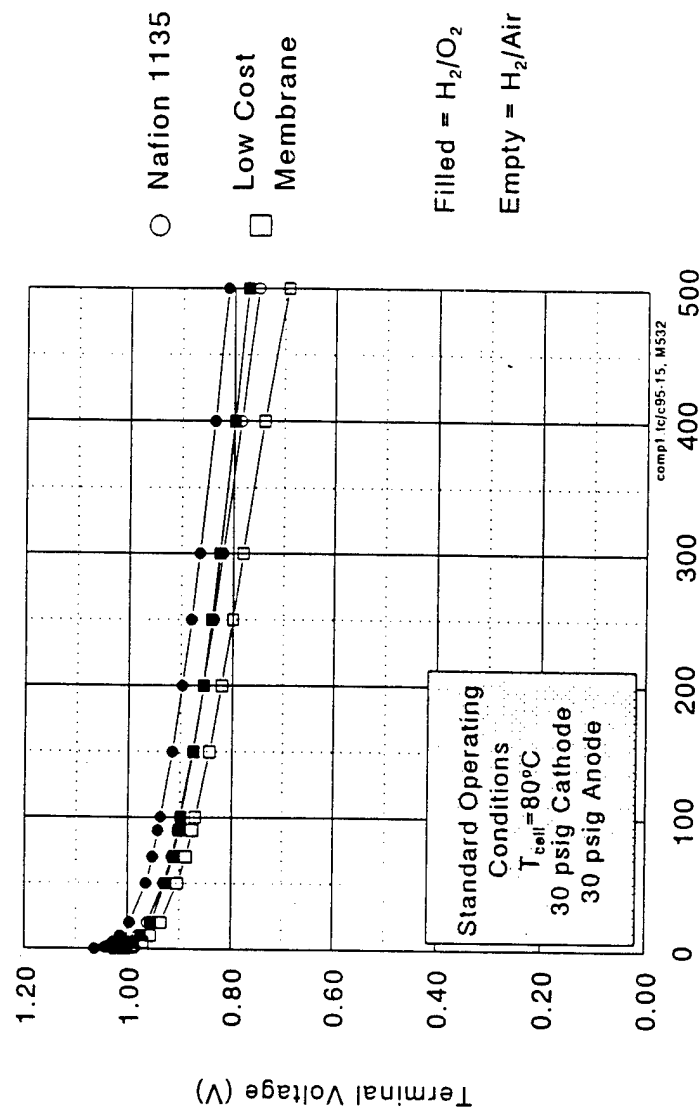
Figure 11. Comparative PEMFC Performance (80°C)

Giner, Inc.

Membrane Comparison
Std Pt Black Anode & Cathode

○ Nafion 1135

□ Low Cost Membrane

Filled = H₂/O₂

Empty = H₂/Air

$T_{cell} \approx 60°C$
Ambient Cathode
Ambient Anode

Terminal Voltage (V)

Current Density (mA/cm²)

comp2.lc/c95-15, M532
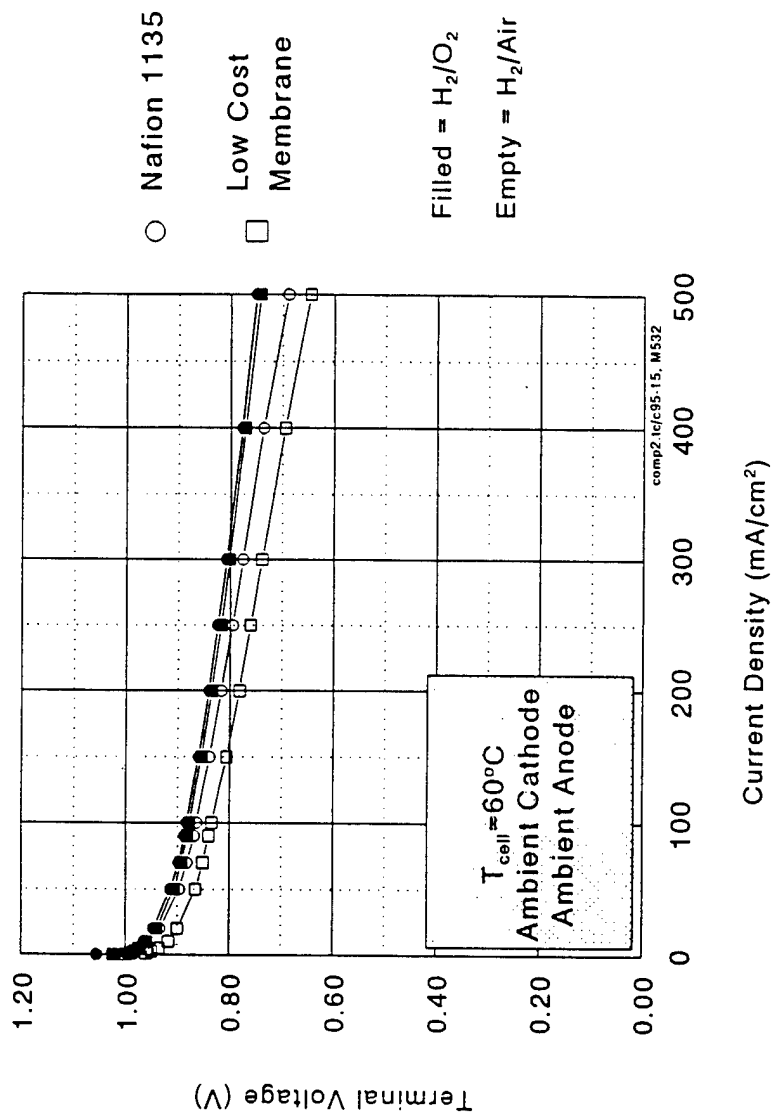
Figure 11 (cont.) Comparative PEMFC Performance (60°C)

Giner, Inc.

Membrane Comparison
Std Pt Black Anode & Cathode

○ Nafion 1135

□ Low Cost Membrane

Filled = H_2/O_2

Empty = H_2/Air

Terminal Voltage (V)

1.20
1.00
0.80
0.60
0.40
0.20
0.00

$T_{cell} \approx 40°C$
Ambient Cathode
Ambient Anode

0   100   200   300   400   500

Current Density (mA/cm²)

comp3.1c/c95-15, M532

Figure 11 (cont.) Comparative PEMFC Performance (40°C)

INNOVATIVE APPROACHES FOR FUEL CELLS

Oliver J. Murphy
Lynntech, Inc.
7610 Eastmark Drive, Suite 105
College Station, TX 77840

At present, various primary and secondary batteries are used by the Army to provide portable and mobile power for electronic equipment in the battlefield environment. These battery power sources have been developed for many decades and, for the most part, have gained wide acceptance by Army personnel. However, they suffer from a number of drawbacks that has led the Army to investigate the development of alternative power source technologies. Resupply of both primary and secondary batteries, along with recharging secondary systems, are major problems in a dynamic battlefield theater. Since many battery chemistries contain toxic and hazardous chemicals, safety and disposal of these power sources are major issues faced by the A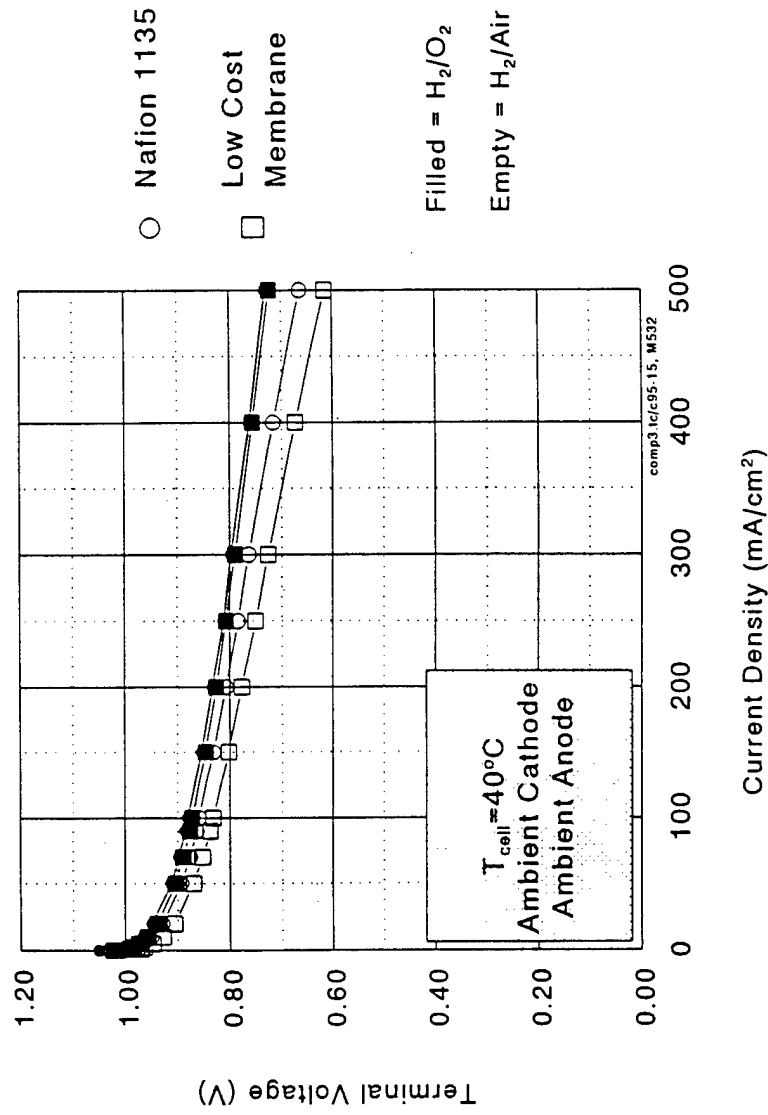rmy. In addition, the cost associated with these power sources, both for military exercises and actual engagements, are becoming prohibitive in an era of shrinking military budgets.

An alternative to batteries, both from a performance and cost consideration, can be provided by fuel cell power sources. Batteries store their energy usually in the form of active solid masses attached to current collector electrodes within the battery container. On discharge (and, subsequently, on charge for secondary systems) the active chemical masses at each electrode are transformed from one crystal structure to another. This often limits the power that can be delivered by the battery and/or the number of charge/discharge cycles. Where a charge or discharge product at a battery electrode forms an electrolyte-soluble species, detrimental affects on performance, e.g., shape change, dendrite growth, etc., can result. In the case of fuel cells, chemical energy storage is physically separated in the power system from the actual energy conversion device itself. Thus, reuse of a fuel cell power source can simply be achieved by replacing the spent chemical energy storage container. Hence, the use of fuel cell systems as power sources should give rise to a considerable reduction in cost and greatly simplify logistics in the battlefield environment.

In the development of fuel cell power sources over the years, the goal has been to produce systems having extended operating lifetimes, e.g., thousands to tens of thousands of hours for applications such as electric vehicles and dispersed power plants in urban areas. To achieve these lifetimes, the materials that can be used are restricted and, in many cases, are exotic and expensive. Further, issues such as stack design, manufacturing or quality assurance become critical. However, on considering fuel cells as disposable portable and mobile power sources for the Army, material components and system integration become issues that should be addressed. Thus, the purpose of this presentation is to outline innovative approaches for fuel cells in the context of disposable fuel cell power sources that are relevant to the Army.

On considering fuel cell power sources that could be disposable, some primary issues that need to be taken into account are outlined in Figure 1. If a simple set of mission requirements/fuel cell system performance characteristics are considered (cf., Fig. 2), potential candidate fuel cell systems include: ion exchange membrane fuel cells (IEMFCs); alkaline fuel cells (AFCs), and biological fuel cells (biofuel cells). For the selected candidate fuel cell systems, potential fuel/oxidant couples are listed in Figure 3. Of the potential fuels hydrogen, methanol, and logistical materials (food, organic waste, vegetable matter, diesel, and JP-8) seem to be the most suitable and attractive. The most desirable oxidants include air or compressed pure oxygen with concentrated aqueous hydrogen peroxide solutions being of secondary importance.

In the case of an alkaline fuel cell, component material/system integration issues are outlined in Figure 4. It is proposed that an immobilized alkaline electrolyte would be the most

appropriate. Thus, non-carbon containing fuels and air which has carbon dioxide scrubbed from it can only be used. For such small alkaline fuel cells, the major issue that needs to be addressed is product water removal. The attractiveness of an alkaline fuel cell system over a corresponding acid-based system is that it gives rise to the selection of a wide variety of materials of construction. In addition, the performance of alkaline fuel cell systems, as demonstrated at least by expensive aerospace systems, is superior to that derived from acid-based fuel cell systems.

The use of solid ion exchange membranes as electrolytes in fuel cells considerably reduces the complexity in fabricating such systems. Fully fluorinated ion exchange membranes both in the cationic (H^+) and anionic (OH^-) from having long lifetimes, even at elevated temperatures, are commercially available (cf., Fig. 5). However, because of their extremely high cost per unit area, alternative ion exchange membranes, either partially fluorinated or hydrocarbon-based, need to be developed. Desired characteristics of new membrane electrolytes include: (i) thin membranes with improved mechanical properties and higher conductivities; (ii) inhibition of the crossover of liquid organic fuels (e.g., methanol) from the anode to the cathode. Alternative proton exchange membrane electrolytes that are presently being explored are described in Figure 6.

The performance characteristics of proton exchange membrane fuel cell supplied with hydrogen-air as reactants is presented in Figure 7. Examination of the data shown in the figure demonstrates that such a fuel cell system can yield high power densities. The performance of a similar proton exchange membrane fuel cell supplied with methanol-oxygen as reactants is illustrated in Figure 8. While giving a lower power output the liquid fed aqueous methanol system is very attractive as the basis of portable and/or mobile power sources for the Army.

For proton exchange membrane fuel cells, anode electrocatalysts containing low platinum loadings or which are based on non-noble metals, e.g., WC, are highly desirable. This is particularly relevant in the case of the direct methanol fuel cell. As cathode electrocatalysts, binary or ternary platinum-based alloys, transition metal macrocyclics and Chevrel compounds (e.g., $Mo_2Ru_4Se_8$) can be used. For the best performance, it is necessary to optimize electrocatalyst layers and catalyst support layers for liquid and gaseous reactants. Anode electrocatalysts that are CO-tolerant and that readily oxidize intermediates formed during the oxidation of simple organic fuels need to be developed. Further, organic fuel-tolerant electrocatalysts for the cathodic oxygen reduction reaction need to be identified (e.g., $Mo_2Ru_4Se_8$).

To take advantage of simple manufacturing methods and, hence, lower the cost of proton exchange membrane fuel cell stacks, novel bipolar plate/flowfield configurations need to be utilized. Unitary structures consisting of: (i) expanded Ti/Ti sheet/expanded Ti; (ii) metal foam/Ti sheet/metal foam; and (iii) metal foam/polymer-filled metal foam/metal foam are presently being developed at Lynntech. The polymer filled metal foam functions as a barrier to prevent reactant gas mixing but can be selected to allow transport of water from the cathode side to the anode side in a proton exchange membrane fuel cell. Bipolar plate/flowfield configurations derived from these unitary structures possess a number of desirable characteristics (i) multifunctional capability (good electronic conductivity, reactant barrier properties, and facilitate internal humidification/water management); (ii) lightweight, simple construction with excellent mechanical properties; and (iii) aid in obtaining uniform temperature profiles across the face of an electrode. For short lifetime (less than or equal to 500 hours) disposable proton exchange membrane fuel cells, plastics of lightweight metals (e.g., aluminum or magnesium alloys) suitably surface treated can be used for cell frames. For the development of lightweight, small volume fuel cells at Lynntech, conventional end plates and tie rods are being replaced with either aluminum honeycomb or carbon/carbon composites where the stack is held together by means of polymer strapping material.

For a disposable fuel cell having a power output of less than or equal to 10 Watts, biofuel cells may provide an attractive long-term option. Such systems are neutral saline solution

containing a redox mediator (e.g., thionine, 2-hydroxyl-1,4 naphthoquinone (HNQ)) as the electrolyte. The anode biocatalyst could consist of individual redox enzymes of whole cells immobilized in a support matrix. Reticulated vitreous carbon, carbon foam or carbon cloth could be used as current collectors. Carbon-supported platinum (or manganese dioxide) deposited on a gas diffusion electrode substrate and subsequently hot pressed to an ion exchange membrane could function as the cathode electrode structure utilizing oxygen from the air as reactant. A stacked arrangement of biofuel cells is shown in Figure 9. Since the current density obtained from such fuel cell systems is low, edge current collection can be employed eliminating the need for bipolar plates. The walls of each cell housing can be fabricated using a conventional polymeric material that avoids the use of cell frames. Thermal and water management for biofuel cells are not an issue since these systems are low power output devices. The major attraction of the biofuel cell for the Army is that the fuel used either by organic wastes, carbohydrates, plant material, hydrocarbons or alcohols.

On considering disposable fuel cell power sources for the Army, manufacturability/cost factors must be considered. Thus, the machining of parts or the use of other time intensive procedures should be avoided. Fabrication steps involved molding, casting, or stamping should be explored where possible. Readily available plastics and metals should be used as materials of construction. In order to avoid environmental impact during fuel cell operation, materials used for the fabrication of containers required for the storage and handling of fuels and oxidants should be compatible with the environment on being disposed of and should readily degrade and/or corrode in the ground. Byproducts of fuel and/or oxidant generation as well as those arising from electrochemical reactions in a fuel cell should be environmentally friendly. On disposing of an actual fuel cell power source after its useful lifetime has been exceeded, materials used in its construction must not contaminate the soil or ground water. Biodegradable polymers and readily corrodible, lightweight metals are highly desirable as materials of construction. Non-controlled disposal of unconsumed potentially toxic fuels or oxidants should be prevented. In order to have the required reliability/lifetime characteristics, disposable fuel cell power sources must exhibit a shelf life in the deactivated state of the order of a few years.

INNOVATIVE APPROACHES FOR FUEL CELLS

LYNNTECH, Inc.

PRIMARY ISSUES

- MISSION REQUIREMENTS/FUEL CELL SYSTEM PERFORMANCE

- FUEL/OXIDANT COUPLE(S)

- COMPONENT MATERIALS/SYSTEM INTEGRATION

- MANUFACTURABILITY/COST

- ENVIRONMENTAL IMPACT (DURING OPERATION AND ON DISPOSAL)

- RELIABILITY/LIFETIME (SHELF LIFE AND OPERATING LIFE)

- SAFETY/TOXICITY

- ATTITUDE INDEPENDENT OPERATION

- CLIMATIC EFFECTS ON PERFORMANCE

INNOVATIVE APPROACHES FOR FUEL CELLS

MISSION REQUIREMENTS/FUEL CELL SYSTEM PERFORMANCE

- POWER OUTPUT: 50 - 1,000W

- MISSION LIFETIME: $\leq$ 500 hours

- OPERATING TEMPERATURE: $\leq$ 85°C

- REACTANT PRESSURES: $\leq$ 30 psia

CANDIDATE FUEL CELL SYSTEMS

- ION EXCHANGE MEMBRANE FUEL CELLS (IEMFCs)

- ALKALINE FUEL CELLS (AFCs)

- BIOLOGICAL FUEL CELLS (BIOFUEL CELLS)

LYNNTECH, Inc.

INNOVATIVE APPROACHES FOR FUEL CELLS

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LYNNTECH, Inc.

INNOVATIVE APPROACHES FOR FUEL CELLS

FUEL/OXIDANT COUPLES FOR CANDIDATE FUEL CELL SYSTEMS

POTENTIAL FUELS

- HYDROGEN
  chemical hydrides, compressed hydrogen gas, and reformate (integrated fuel cell-reformer)

- METHANOL

- HYDRAZINE

- OTHER SIMPLE ORGANIC COMPOUNDS
  trimethoxymethane, formaldehyde, formic acid

- LOGISTICAL MATERIALS
  food, organic waste, vegetable matter, diesel, and JP-8

POTENTIAL OXIDANTS

- OXYGEN (FROM THE AIR)

- COMPRESSED PURE OXYGEN

- HYDROGEN PEROXIDE

- NITRIC ACID

- OXYANIONS OF CHLORINE IN THE ACID FORM
  hypochlorous acid (HClO) and chlorous acid (HClO$_2$)

INNOVATIVE APPROACHES FOR FUEL CELLS

COMPONENT MATERIALS/SYSTEM INTEGRATION

ALKALINE FUEL CELL

- **ELECTROLYTE**

  Matrix supported potassium hydroxide (30-45 wt % KOH)

  Reconstituted asbestos matrix

  Potassium titanate matrix

- **ANODE ELECTROCATALYSTS**

  Carbon-supported palladium or platinum (0.72 mg cm^{-2}), Raney nickel, 80% Pt/20% Pd

- **CATHODE ELECTROCATALYSTS**

  Silver, metal oxides of perovskite structure, transition metal macrocyclics, platinum, 90% Au/10% Pt

- **BIPOLAR PLATE**

  Gold-plated magnesium, graphite

- **CELL FRAMES**

  Plastic (polysulfone)

- **CARBON DIOXIDE REMOVAL FROM AIR**

  Alkali absorption, adsorption in molecular sieves, soda lime (CaO)

- **THERMAL MANAGEMENT AND WATER REMOVAL**

  Air cooled

  Water removal needs to be addressed

INNOVATIVE APPROACHES FOR FUEL CELLS

COMPONENT MATERIALS/SYSTEM INTEGRATION

ION EXCHANGE MEMBRANE FUEL CELLS

- **MEMBRANE ELECTROLYTES**

  Cation (H^+; Nafion®) and anion (OH^-; Tosflex®)

  Other fully fluorinated proton exchange membranes include: Aciplex® S and GoreSelect®
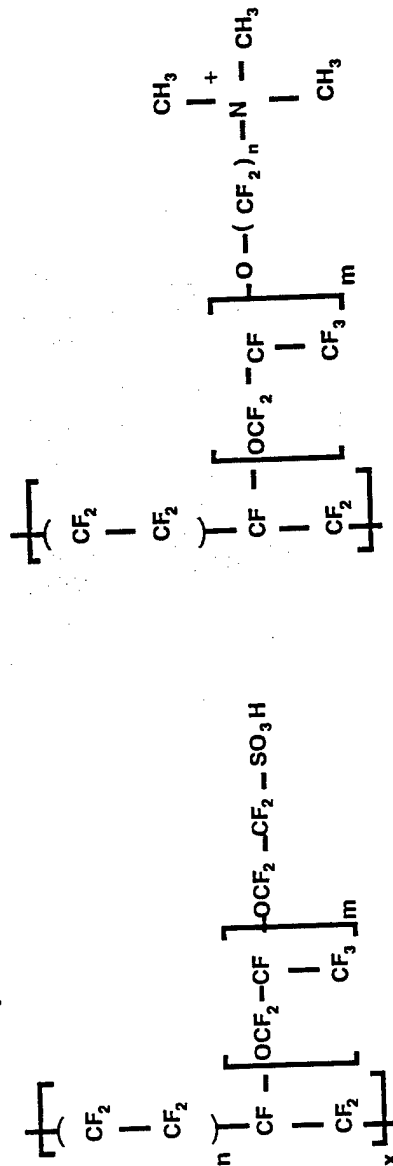
Alternative proton exchange membranes are either partially fluorinated or hydrocarbon-based containing stable aromatic ring structures, e.g., crosslinked polystyrene sulfonic acid (30 wt%)/polyvinylidene fluoride (70 wt%) (PSSA/PVDF), sulfonated rigid rod polyphenylenes, and a trifluorostyrene-based material

Membrane Characteristics

Need liquid water to be conductive

Crossover of liquid organic fuels (e.g., methanol) from anode to cathode takes place

Thin membranes with improved mechanical properties and higher conductivities are needed

LYNNTECH, INC.

INNOVATIVE APPROACHES FOR FUEL CELLS

COMPONENT MATERIALS/SYSTEM INTEGRATION

ION EXCHANGE MEMBRANE FUEL CELLS

- **ALTERNATIVE MEMBRANE ELECTROLYTES**

  The third generation Ballard membrane is based on trifluorostyrene (TFS) and has the structure shown below, where the groups labeled A_1 through A_3 are some combination of perfluoroalkyls, partly fluoroalkyls, and aromatic groups. The exact combination has not been publicly described.
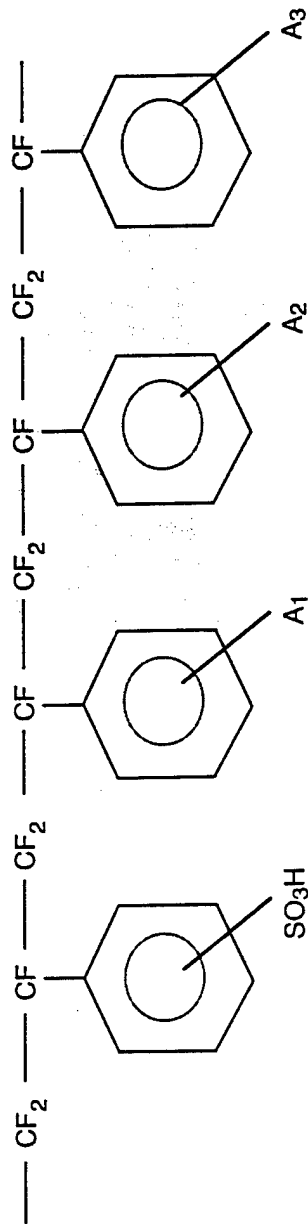
Basic structural unit of proposed sulfonated rigid rod polyparaphenylene
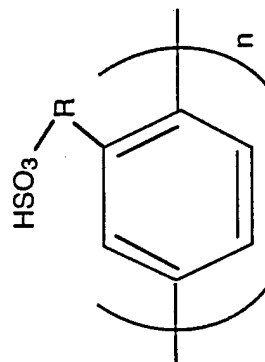
INNOVATIVE APPROACHES FOR FUEL CELLS

Hydrogen - Air Fuel Cell Performance
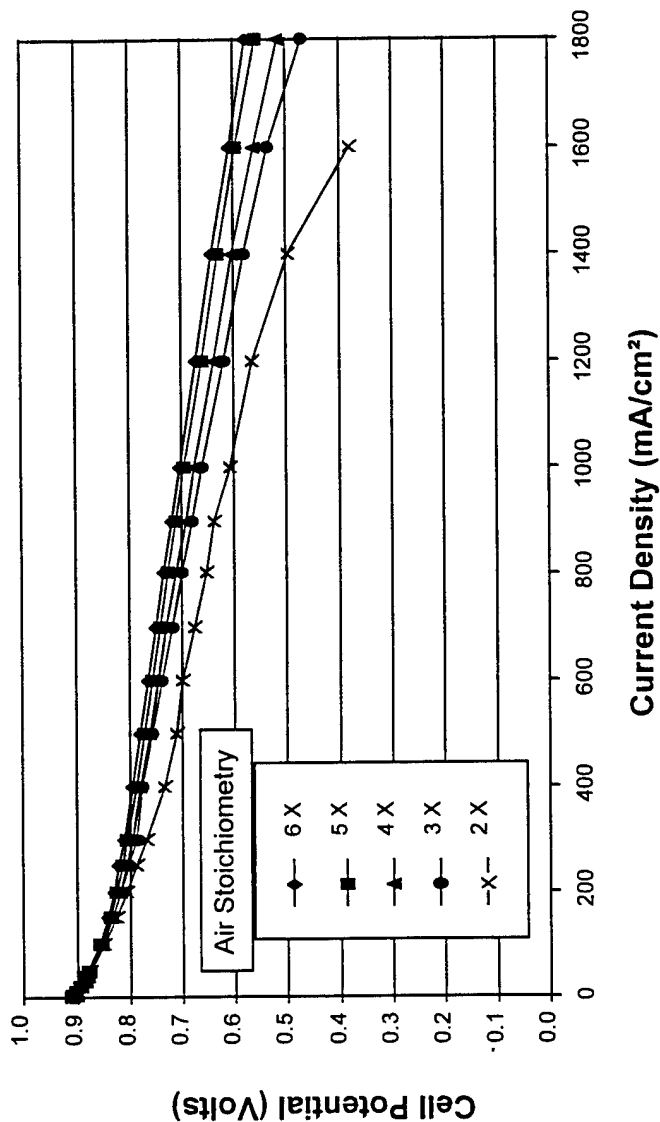
Experimental Conditions

T_{cell} = 65°C
14% Relative Humidity
Anode: 0.35 mg/cm² supported Pt
Cathode: 1.7 mg/cm² Pt black

Membrane: Gore Select® 20 μm
Air backpressure = 15 psig
H_2 backpressure = 15 psig
H_2 stoichiometry = 2 X

Air Stoichiometry
- 6 X
- 5 X
- 4 X
- 3 X
- 2 X

LYNNTECH, Inc.

INNOVATIVE APPROACHES FOR FUEL CELLS

Methanol - Oxygen Fuel Cell Performance

Methanol Concentration (M)
- ◇— 0.5 M
- □— 1 M
- △— 2 M
- ✕— 3 M

Current Density (mA/cm²) vs **Cell Voltage (V)**
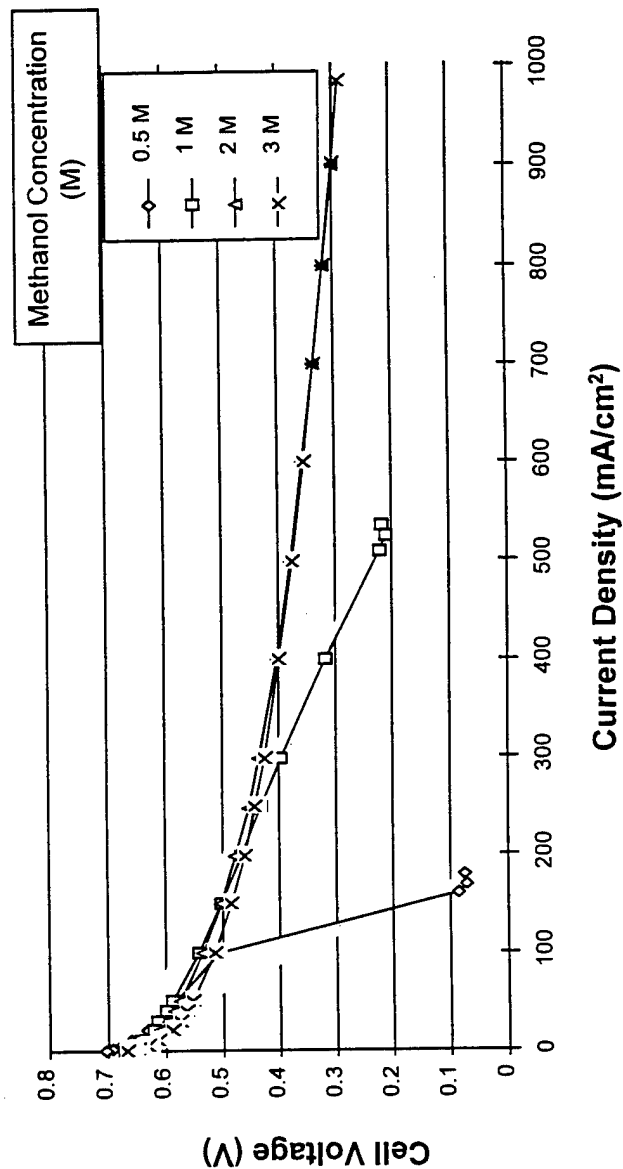
Experimental Conditions

T_{cell} = 80°C
Anode: 4 mg/cm² unsupported Pt-Ru
Cathode: 4 mg/cm² unsupported Pt
Membrane: Nafion® 112

O_2 flow rate = 3.9 L/min
O_2 backpressure = 30 psi
Methanol Flow Rate = 8 mL/min
Methanol Pressure = 30 psi

LYNNTECH, Inc.

INNOVATIVE APPROACHES FOR FUEL CELLS
COMPONENT MATERIALS/SYSTEM INTEGRATION
BIOFUEL CELLS

LYNNTECH, Inc.

O₂

O₂

O₂

O₂

O₂

O₂

divider

cathodes

divider

CELL 1

CELL 2

CELL 3

CELL 4

anode

nutrient/redox mediator
diffusion channels

Conducting particles
(anode current collector)

Immobilized
biocatalyst

porous sol-gel
support matrix

PERSON-PORTABLE FUEL CELLS AT IFC

Donald L. Maricle
195 Governors Highway
South Windsor, CT 06074

Introduction

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H_2/O_2

The Soldier Cooling Power Module (SCPM) program is developing at H_2/O_2 based fuel cell system to achieve the CECO goal of 10 pounds, 150 watts, and 1200 watt-hours. The SCPM design couples IFCs passive-water management cell technology and commercial high performance filament wound hydrogen and oxygen storage tanks. The safety and simplicity of the design is enhanced by near ambient pressure stack operation, and the passive water management system which both removes product water and humidifies incoming gas streams. A circular plan form, and simple cooling fin cell design, allows rejection of stack waste heat to ambient with only a light weight external fan. Operation is independent of attitude or gravity and requires no water pumps or external humidifiers. The result is a highly efficient, 24-volt fuel cell battery with recharge capability.

The program has progressed through the point of stack design verification with a half-stack qualification test. Instant start capability, load transient from open circuit to full power and acceptable thermal and water management were demonstrated. Commercial-off-the-shelf reactant storage tanks, and gas pressure staging and supply components have been procured. Demonstration testing of a 330 watt-hour off-the-shelf component version is schedules for mid 1996.

DMFC

The ARPA supported DMFC program is also focused on building a 150-watt demonstrator in mid 1996. The conceptual design shows a 600-watt hour unit weighing about 11 pounds. The application is again person portable power fuel soldier systems. In the DMFC case, however, several technological limitations are being pursued in parallel with the hardware demonstration. Team members are participating in the technology development effort. The issues currently being addressed, are: a low crossover membrane (DuPont), a higher activity DMFC anode catalyst (ICET, LANL), and a methanol tolerant cathode catalyst (CWRU).

Current IFC DMFC cell technology employs a Pt/Ru anode, a Pt black air cathode, and Nafion 117 membrane. Single cell performance of 0.4 V at 200 ASF, 180°F, 3,000 ccm dry air, 3 ccm 1 M MeOH, has been demonstrated in a 5 in^2 cell. At the 200 ASF design point methanol crossover (measured by CO_2 analysis at the cathode exit, corrected for crossover of product CO_2 from the anode) is ~ 100 equivalent ASF. This provides a calculated overall system efficiency of 20% electrical.

The 150-watt demonstrator stack hardware is based on the circular H_2/O_2 design modified for liquid feed methanol/air. The system includes a single exit condenser to recover water and methanol from the combined anode and cathode exhausts. The condensables and makeup methanol is returned to the anode. A small air blower and liquid pump complete the major system components. The exit condenser controls the water balance in the system, allowing the stack operating temperature to be optimized for performance.

The ARPA DMFC program at IFC is presently addressing two issues; optimizing DMFC performance in the circular cell hardware and developing a cathode configuration which will support operation at 50% air utilization (electrochemical + crossover) in the presence of crossover methanol. The utilization requirement is set primarily by the need to maintain water balance in high ambient temperature environments (thermal pinch at the exit of the water recovery condenser). A power module demonstration is planned for mid 1996.

Disposable Fuel Cells

Disposable fuel cells is a concept contrary to the mind set of most fuel cell developers. Typically considerable development effort is expended to ensure sufficient stack and system lifetime to satisfy application requirements and minimize life cycle costs. However, following are few thoughts regarding how a life requirement of only 500 hours might enable previously discarded concepts to be implemented.

For PEM-based fuel cells with only a 500-hour life requirement, unprotected stainless steel foil might suffice for separator plates. This could save weight, save cost, and facilitate stamped flow fields. Shelf life might be an issue.

The major limitation of direct methanol cell technology is presently methanol crossover. There is evidence that sulfonated polystyrene in a polyvinylidene fluoride matrix (USC - S. Prakash) or a styrene/ethylene/butylene tri-block (DAIS - Tim Tangredi) offers substantially lower methanol crossover than Nafion 117. An issue with these sulfonated hydrocarbon membranes is stability. The low crossover and potentially low cost of these materials may be accessible in a disposable DMFC fuel cell with a lifetime requirement ≤ 500 hours without solving a life problem.

Perhaps the most useful option for disposable fuel cells is to reconsider the use of base electrolytes for H_2/air stacks. It is well known that most fuel cell developers abandoned this approach by the 60s due to carbonation of the electrolyte by residual CO_2 in the atmosphere. Trapped liquid KOH (as used in IFCs H_2/O_2 space power plant) is one obvious possibility. However, another option for a short lifetime fuel cell may be an anion exchange membrane in the OH^- form. These basic membranes have generally not shown sufficient stability for fuel cell use. However, this may bear re-examination under the 500-hour life limit guidelines.

The advantages of an OH^- electrolyte are well known. O_2 reduction kinetics are much faster in base. This improves performance of air electrodes. Another option available in base electrolytes is the use of macrocyclic cathode catalysts. This would help eliminate the need to recycle noble metal containing electrodes from disposable cells.

Another old concept which might be revisited in this context is the use of hydrazine as a fuel. Hydrazine provides a lower electrooxidation overvoltage (close to H_2) than methanol, and higher practical specific energy density than H_2 in pressure tanks. For example, H_2 at 2% loading in a pressure tank might provide 375 Whr/kg where as hydrazine might provide 700 Whr/kg[1]. Furthermore since no CO_2 is produced at the anode, base electrolytes can be used to improve the kinetics of both the hydrazine anode and the air cathode.

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Concerns about the cost, toxicity, and explosion hazards of hydrazine have discouraged development. Again the disposable concept may ameliorte some of these concerns. A "hydrazine/air battery" might store the liquid hydrazine as an aqueous solution in each anode compartment with no refueling capability. This would minimize human exposure to the fuel and reduce the explosion hazard. A requirement to discharge the unit prior to disposal might reduce the hydrazine level to tolerable limits.

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DESIGN PHILOSOPHY FOR LIGHT WEIGHT PEM H_2/O_2 SYSTEMS

- Simple (no moving parts) system keeps weight down and reliability up

- IFC passive water removal technology uses only a low ΔP available from reactant gases to manage product water

- Circular planform simplifies seals and facilitates external cooling

SOLDIER COOLING POWER MODULE (H_2/O_2)

- ## Objective
  - Design, build, demonstrate, power module
    - H_2/O_2 PEM
    - 150W, 24 volts, 900 Whr
    - $\leq$10 LB, 600 in^3

- ## Approach
  - Develop/verify lightweight PEM H_2/O_2 stack
  - Procure off-the-shelf tankage and system components

Approach (continued)

- Integrate test and deliver power module

Status

- Half-height PEM stack demonstrated
- Tankage and ancillaries obtained
- Demo fabrication in progress

SOLDIER COOLING POWER MODULE CONCEPTUAL LAYOUT

Power Module

Fuel Module

PEM Fuel Cell
150 watts / 24 volts
17 psia

H2 Purge Valve / Vacuum Breaker

O2 Bleed Orifice

Pressure Gauge

Pressure Gauge

Quick Disconnects

Two Stage Pressure Regulator

Two Stage Pressure Regulator

Manual Shut-off Valve

Manual Shut-off Valve

Rupture Disk

Rupture Disk

High Pressure Reactant Gas Storage Tank

High Pressure Reactant Gas Storage Tank

FCR-13601A

HS96031
962703

SOLDIER COOLING POWER MODULE

150 WATT
SOLDIER COOLING POWER MODULE
COMPONENTS
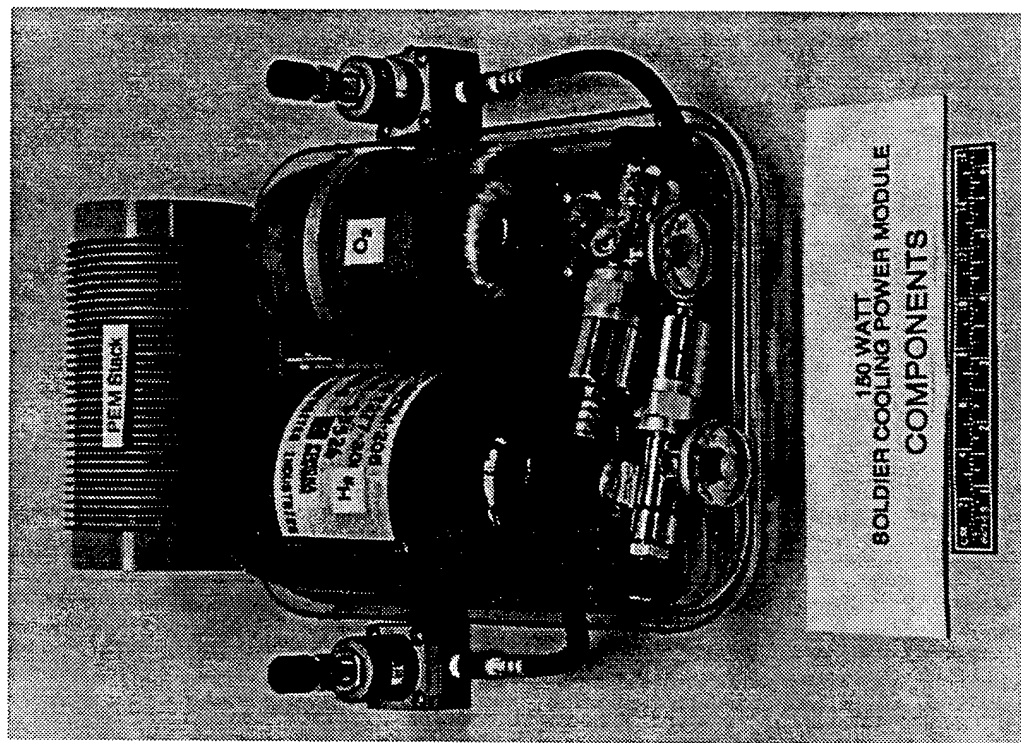
WCN15276

150W SOLDIER COOLING POWER MODULE DEMONSTRATOR

Component	Weight (Lbs)
Cell stack	2.7
H_2 + tank	2.2
O_2 + tank	2.5
Balance of plant	3.6
Total	11.0

CELL PERFORMANCE

BASED ON AVERAGE CELL PERFORMANCE OF 16-CELL STACK

13801-10
950505

CELL VOLTAGE – VOLT

CURRENT DENSITY – AMPS/FT^2
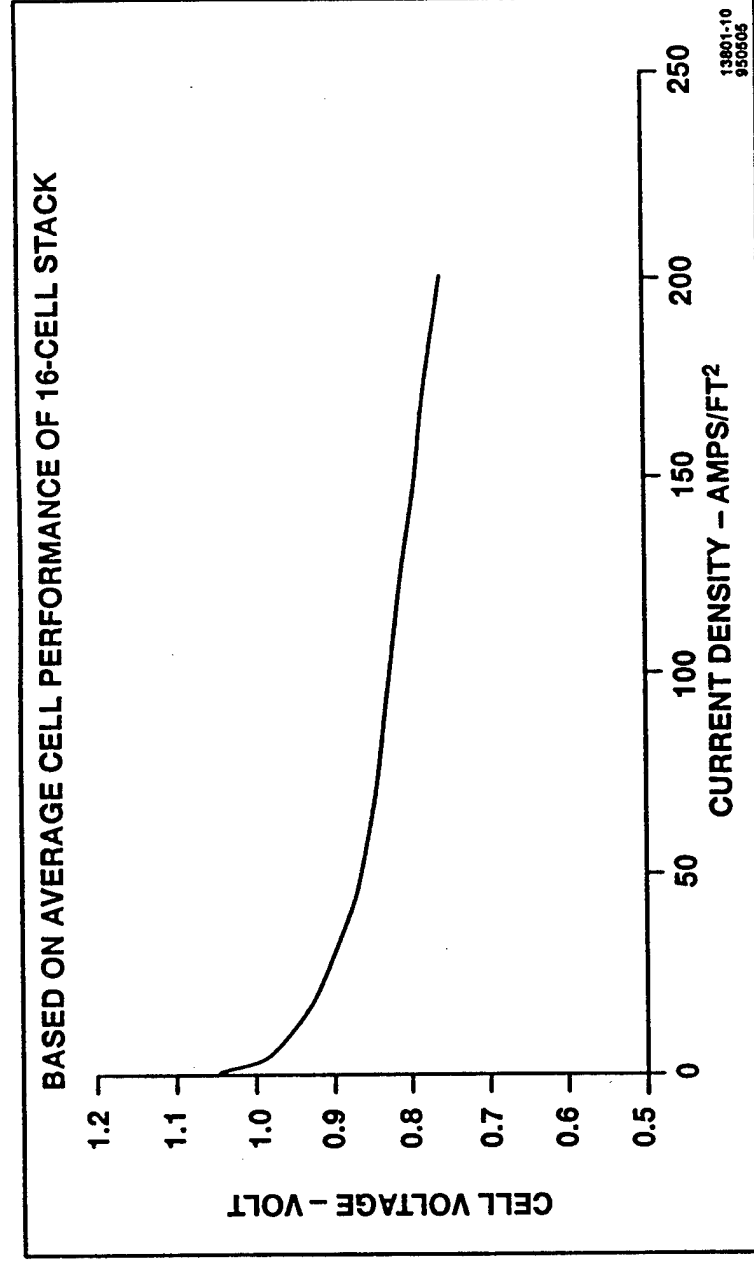
POWER PLANT PERFORMANCE

– Parasite Power = 3 Watts –

STACK VOLTAGE – VOLTS

OUTPUT POWER – WATTS

13801-11
950505
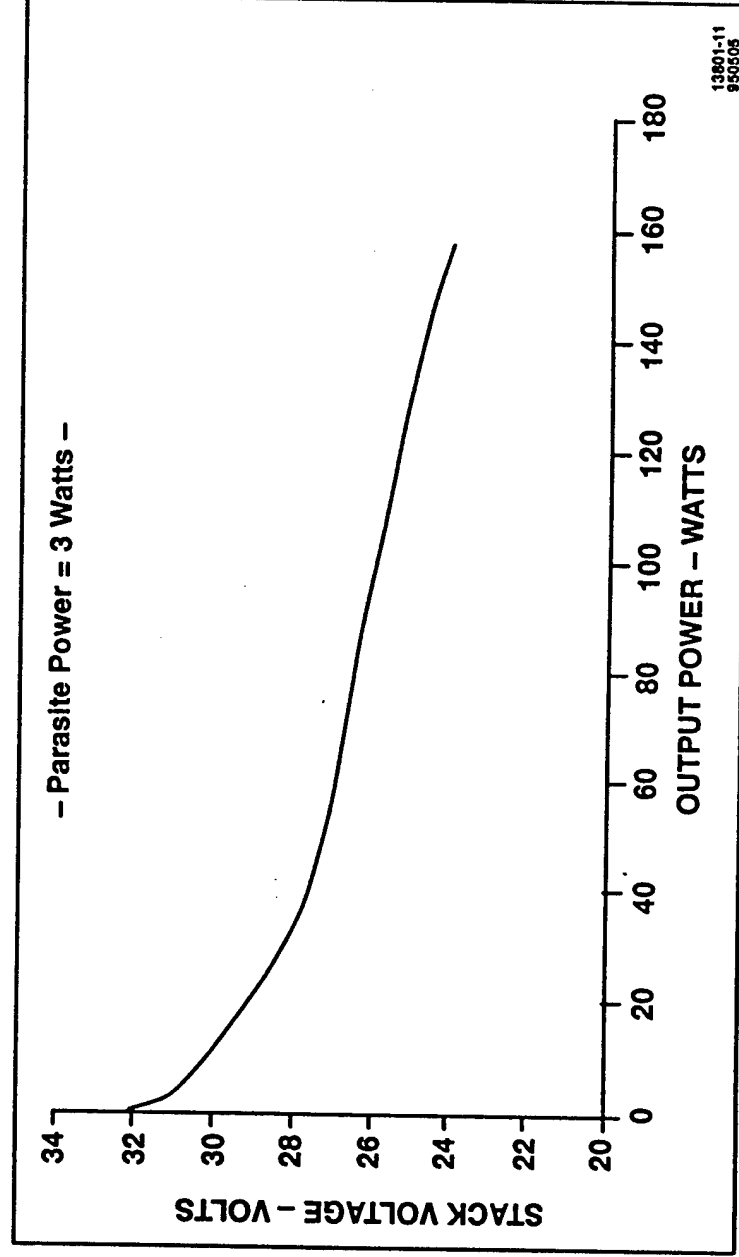
FULL POWER AVAILABLE INSTANTLY
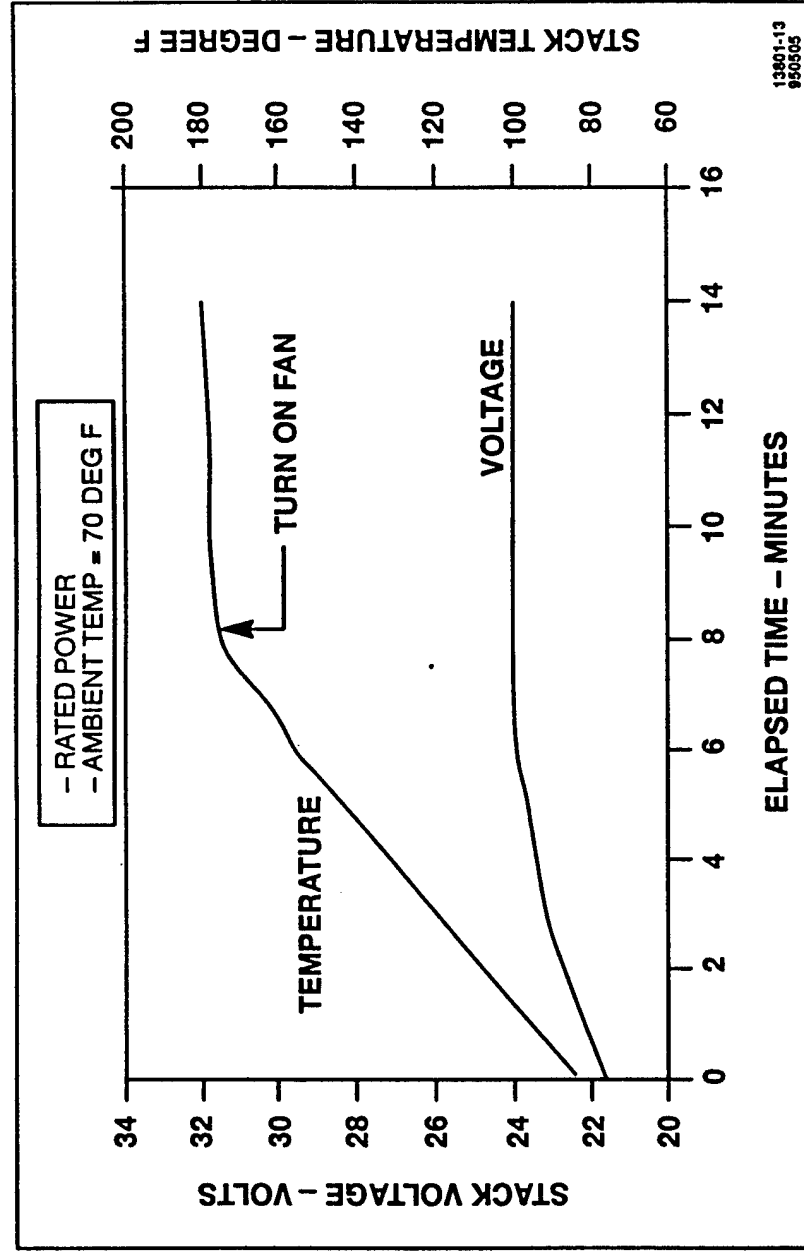
STACK TEMPERATURE – DEGREE F

- RATED POWER
- AMBIENT TEMP = 70 DEG F

TURN ON FAN

VOLTAGE

TEMPERATURE

ELAPSED TIME – MINUTES

STACK VOLTAGE – VOLTS

13801-13
950505

PRESENTATION OUTLINE

- H_2/O_2 - Fuel Cell for Soldier Cooling Power Module

  – CECOM

- **H_2/air - Person Portable Power Options**

- DMFC-Fuel Cell Technology for Person Portable Direct Fuel Cell

  – ARPA/ONR

- Impact of Short Lifetime Requirements on Fuel Cell Barriers

IFC APPROACH TO SMALL H$_2$/AIR SYSTEMS

- Modify cell configuration for air

- Operate at near ambient pressure to simplify system and eliminate transient response issues associated with air compression

PRESENTATION OUTLINE

- H_2/O_2 - Fuel Cell for Soldier Cooling Power Module
  - CECOM
- H_2/air - Person Portable Power Options
- **DMFC-Fuel Cell Technology for Person Portable Direct Fuel Cell**
  - ARPA/ONR
- Impact of Short Lifetime Requirements on Fuel Cell Barriers

150W Soldier Back Pack Program
## Prime: IFC, Team: CWRU, DuPont, ICET, LANL

Program Objectives

- Develop 150W, 600Whr, 24V, direct methanol power module

- Fabricate and test a module meeting the above requirements

Approach

- High Performance Pt/Ru Anode (IFC), (ICET), (LANL)

- Methanol Tolerant O_2 Reduction Catalyst (CWRU)

- Low Crossover Membrane (DuPont)

- Light Weight Stack/System (IFC)

Accomplishments

- Designed power module based on H_2/O_2 circular stack with O-ring seals modified for liquid feed

- Achieved 1 M MeOH/15psia dry air performance of 0.4V/200 ASF using thin film $6mg/cm^2$ cathode

- Circular stack single cell under test

- Methanol crossover analysis modified to account for CO_2 diffusion from anode

- Two types of lower crossover membranes tested
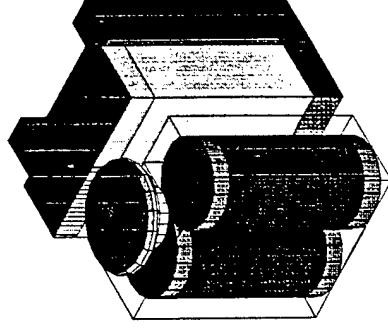
CONCEPTUAL SYSTEM DESIGN

- Two 12V 75W stacks improve packing density

- Condenser recovers water and MeOH, manages water balance, increases stack temperature

- Ducted blower eliminates air flow maldistribution

- Liquid pump mixes recovered water with new methanol and circulates
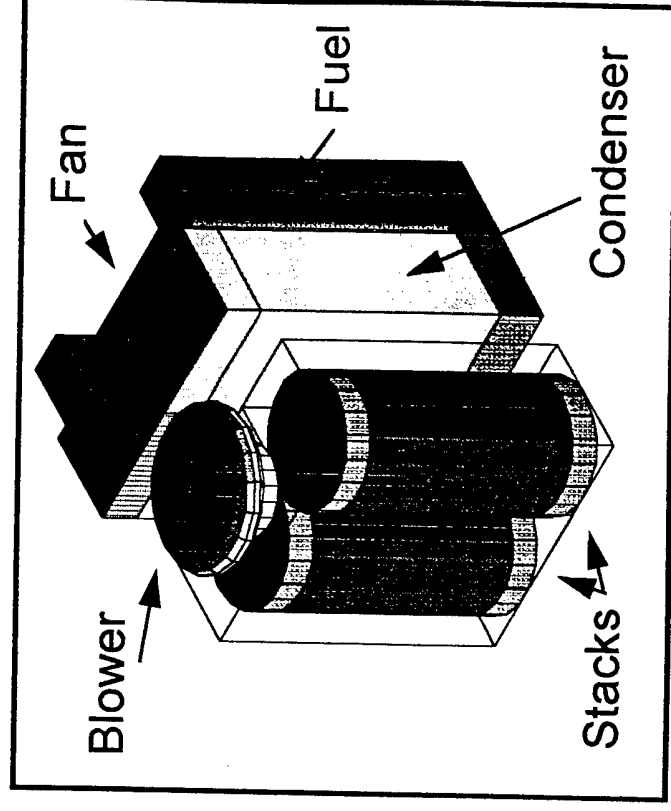
Weights of 600 Whr Components

Component	Weight (LBS)	Volume (in^3)
F/C Stack	5.1	128
Condenser	2.5	66
Process air fan	1.1	25
Cooling air fan	0.8	45
Misc.	0.9	136
MeOH	1.7	
MeOH tank	0.1	59
Totals	12.1	459

CIRCULAR STACK

- Internally manifolded radial liquid feed

- Externally manifolded cross flow air

- Basic stack design proven in H_2/O_2 soldier cooling power module application
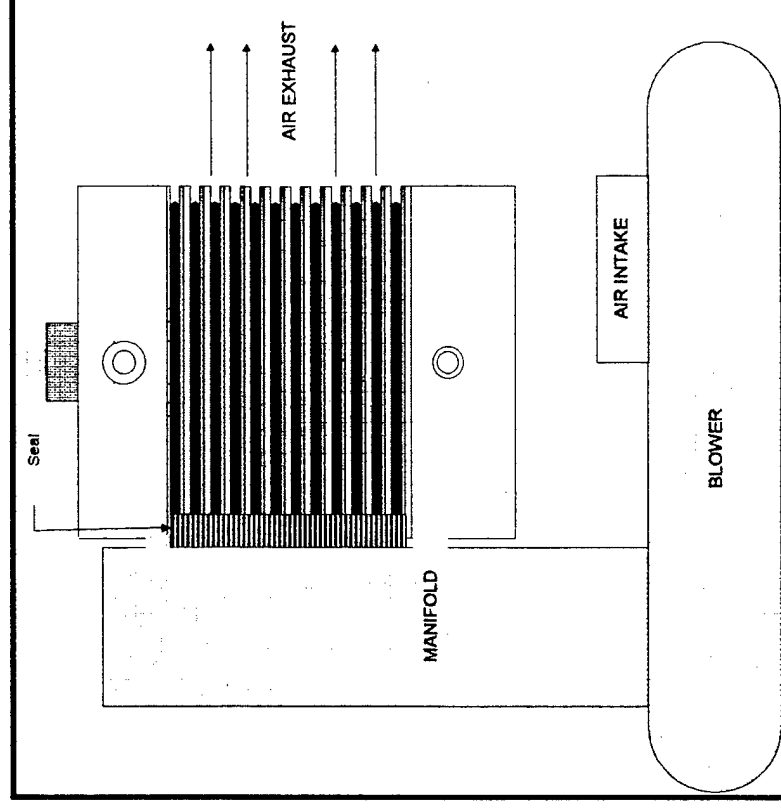
DMFC CELL PERFORMANCE

180°F, 5in² Cell, 3,000ccm Ambient Air/3ccm 1M MeOH

- Anode, 5-6 mg/cm² Pt/Ru black

- Cathode, 5-6 mg/cm² Pt black in all cases

- Nafion added to cathode gave best performance

Cell Voltage (Volts)

0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0

0 100 200 300 400

Current Density (ASF)

—□— Standard   —◆— Nafion impregnated   —▲— Thin film
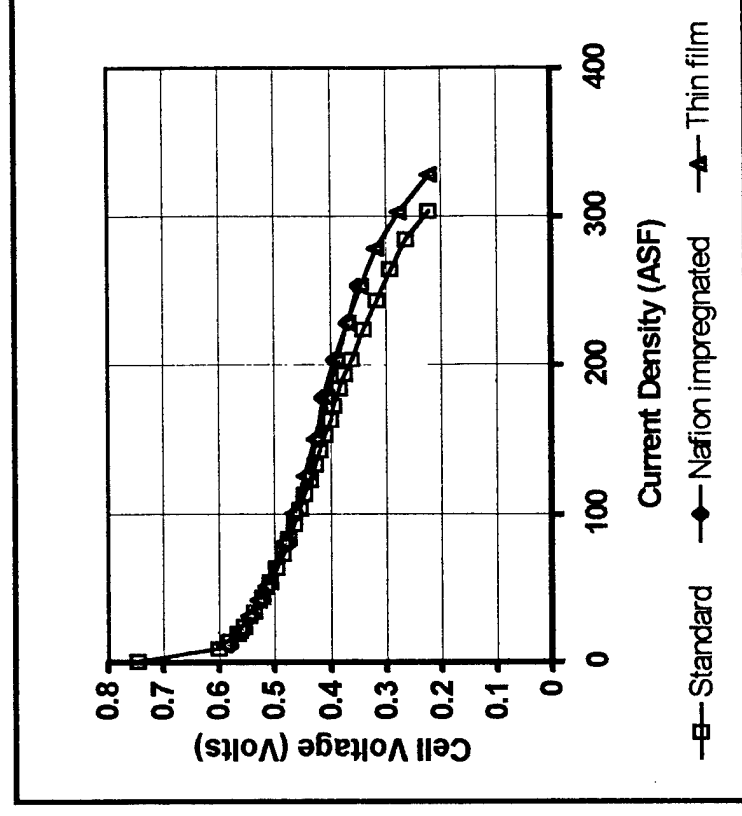
IMPACT OF AIR UTILIZATION
ON PERFORMANCE AND CROSSOVER
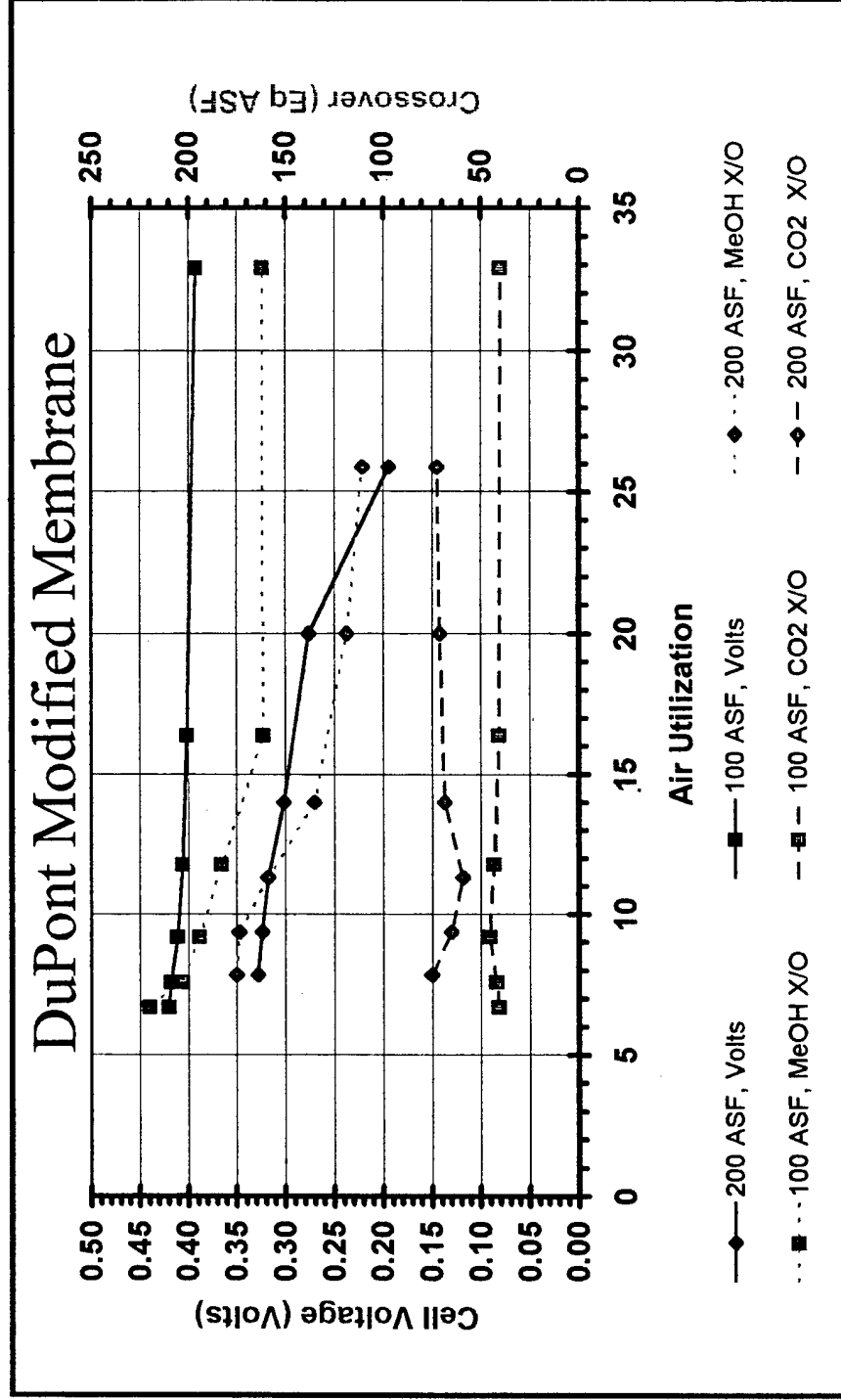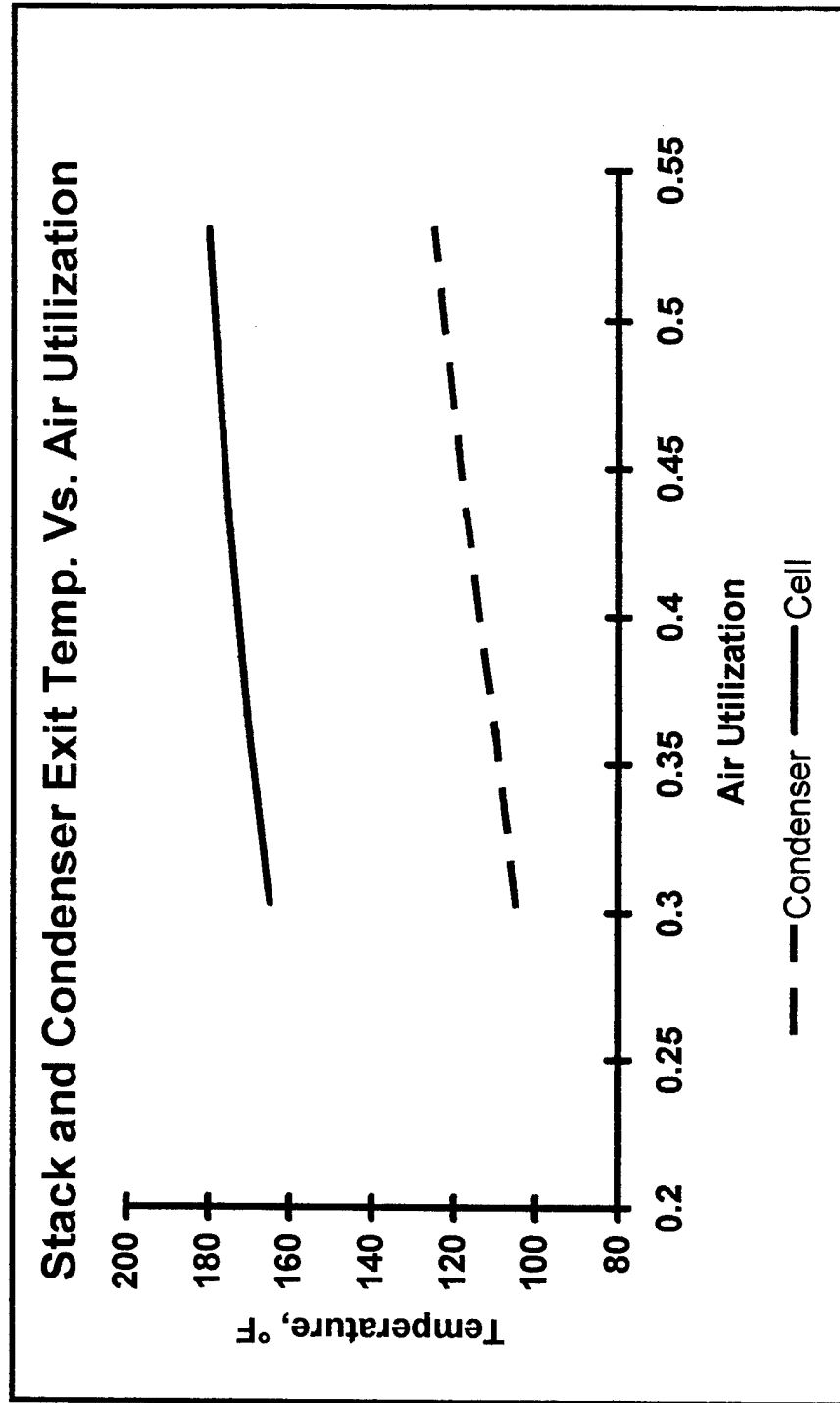
DuPont Modified Membrane

AIR UTILIZATION ISSUE

Stack and Condenser Exit Temp. Vs. Air Utilization

PRESENTATION OUTLINE

- H_2/O_2 - Fuel Cell for Soldier Cooling Power Module
  - CECOM
- H_2/air - Person Portable Power Options
- DMFC-Fuel Cell Technology for Person Portable Direct Fuel Cell
  - ARPA/ONR
- **Impact of Short Lifetime Requirements on Fuel Cell Barriers**

POSSIBLE BENEFITS OF REDUCED LIFETIME REQUIREMENTS

- Cell hardware materials

  – Use stainless foil plates - light, ductile, easy to fabricate, and low cost

- Electrolyte

  – Hydrocarbon H^+ membrane - cheaper, lower MeOH crossover

  – KOH for H_2/air

  – OH^- membranes for H_2/air

BENEFITS (continued)

- Electrodes
  - Low loaded electrodes - cheaper
  - Macrocyclic cathodes - OH⁻ systems
- Fuels
  - $N_2H_4 \cdot H_2O$
    - 700Wh/kg Vs. 375Wh/kg for H_2 at 2% loading
    - High rate anode, useful in OH⁻ electrolytes
    - Toxicity/explosion issues

MICROSCOPIC INVESTIGATIONS OF ELECTRODE STRUCTURE IN FUEL CELLS

William H. Smyrl
Corrosion Research Center
Department of Chemical Engineering and Materials Science
University of Minnesota
Minneapolis, MN

The application of the Confocal Laser-Scanning Microscope (CLSM) to studies of catalysis and electrode structure in fuel cells will be primarily through fluorescence microscopy. A schematic diagram of a CLSM is shown in Figure 1, where several modes of operation are listed. In contrast to a conventional optical microscope where all parts of an object within the field of view are imaged simultaneously, the same image is obtained sequentially using a CLSM. In a CLSM, an image is obtained point by point, whereby only a small part of the object is illuminated. There are a number of significant advantages in using CLSM, e.g., the image is stored digitally and thus can be readily subjected to image processing and image enhancement. More importantly, the use of a focused light source in conjunction with a pinhole aperture in front of the detector allows for a higher depth and lateral resolution than with a conventional optical microscope. The improved lateral resolution results from elimination of the interference of light originating from different points on the object. The main advantage of a CLSM, however, is not in the increased lateral resolution, but rather in its ability to perform "optical slicing". Light originating from planes other than the focal plane is blocked by the pinhole aperture placed in front of the detector. Typical lateral and depth resolutions for a 60x objective lens with a numerical aperture of 1.4 are 0.17 and 0.54 micrometers, respectively. The beam is scanned over a stationary sample, and individual images ("optical slices") are obtained in about one second. This is enabled by moving galvanometer mirrors, by rotating mirror wheels, or by acoustic-optic deflectors. The first technique was used in the microscope used for the results described here.

To illustrate the use of fluorescence mapping with CLSM, we have dissolved fluorescent probes in solutions of Nafion (Dupont) polymer electrolyte and deposited the solution on a carbon surface (highly oriented pyrolytic graphite (HOPG)). As shown in Figure 2, six different probe molecules were used, and deposits of each (in Nafion (Dupont)) were distributed as individual "lines" on the surface. The characteristics of the dyes are listed in Table 1. The individual lines were separated from each other by bare HOPG surface. Light from the CLSM was used to excite fluorescence, and the emitted light was detected after passing through a filter to eliminate the excitation illumination. Of the six fluorescent probes used, two were found to yield high fluorescence (the two rhodamine dyes), one was moderate (fluorescein), and the remaining three had very low fluorescence in the tests. An "optical slice" is shown in Figure 3, where high fluorescence from the rhodamine 6G line is on the left, the fluorescein line is on the right, and the dark region that separates the two is the bare HOPG surface. Rhodamine dyes are cationic and readily partition into Nafion from aqueous solutions. Fluorescein is deposited on the surface of Nafion in contrast. This demonstrates that a dye (such as rhodamine B or rhodamine 6G) dissolved in Nafion (Dupont) can be used to map the location of the polymer electrolyte on a heterogeneous surface. We intend to use the technique to reveal the distribution of Nafion (Dupont) in a membrane electrode assembly of a methanol fuel cell.

The "buried" interface of the membrane electrode assembly can be studied in a half-cell arrangement microscopy can be performed through a Nafion (Dupont) membrane. Optical slicing can be used to determine the distribution of Nafion (Dupont) along the porewalls of the electrode assembly. Use of a second fluorescent dye dissolved in methanol permits concurrent mapping of methanol in the pores of the assembly. Fluorescein is an anion dye that is soluble in methanol, but does not partition into Nafion to the same extent as do cation dyes. The microscopy can be performed with or without current to the electrode assembly and will enable changes in structure
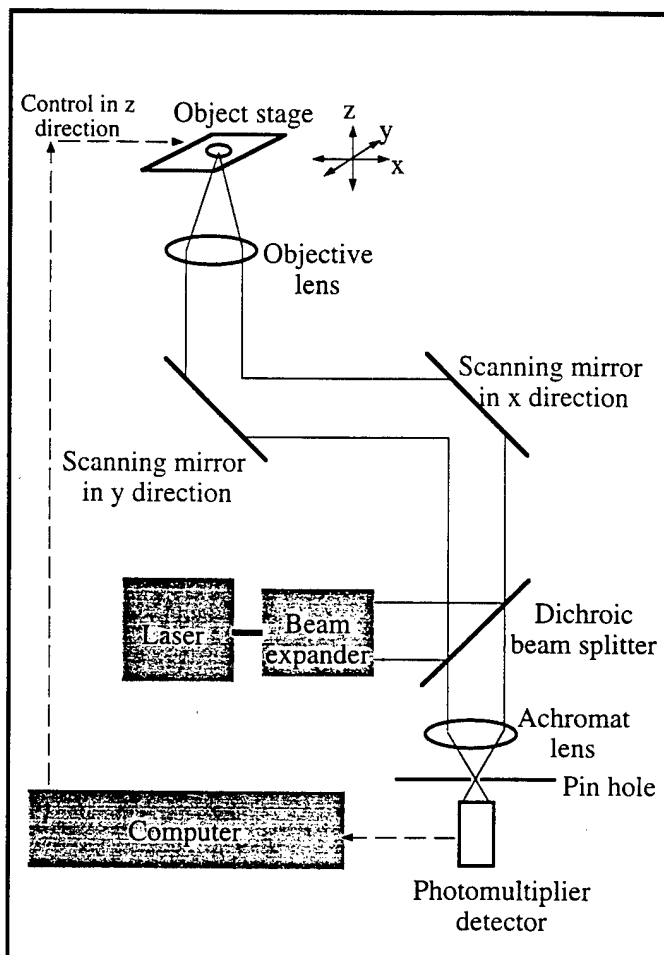
and distribution of components at the electrode/membrane interface. Optical slicing will also be used to determine the depth and distribution of the "reaction zone" at the anode. This is the zone where the catalyst particles, conductive substrate, ionic electrolyte (e.g., Nafion), and the methanol fuel phase are in contact, and where the electrode reaction is concentrated. Simple electrode arrangements will also be investigated in separate studies in order to characterize the efficacy of the techniques. The objective is to use the technique as an <u>in situ</u> tool to enable the development of enhanced electrode structures for the methanol - polymer electrolyte fuel cell. The microscopy study is one component of the current investigations being carried out at the University of Minnesota. Figure 4 identifies the other components of the research program. Professor Kent Mann (University of Minnesota) and his group is investigating molecular catalysts that would enhance or replace the precious metal catalysts for oxidation of methanol. The behavior of the new catalysts will be compared with baseline Pt/Ru catalysts supported on carbon. Professors Ed Cussler (University of Minnesota) and Duward Shriver (Northwestern University) are leading the search for new membranes that would reduce the permeation (crossover) of methanol across the polymer electrolyte fuel cells, and this facilitates the integration of the different components of the research program. Further integration of the research is the objective of Professor David Shores who directs the Exploratory Test Facility. Research by collaborators at the Jet Propulsion Laboratory and at Analytic Power also support the Exploratory Test Facility by fabricating baseline membrane electrode assemblies (MEA).

TABLE 1. FLUORESCENT INDICATORS

Indicator	Excitation Wavelength λ_{max} (nm)	Ionic Form
1. Fluorescein	491	Anion
2. Rhodamine B	543	Cation
3. Crystal Violet	588	Cation
4. Oxazine 4	644	Cation
5. Malachite Green	615	Cation
6. Rhodamine 6G	524	Cation

Figure 1

CONFOCAL LASER SCANNING MICROSCOPE

Control in z direction — Object stage — z y x

Objective lens

Scanning mirror in x direction

Scanning mirror in y direction

Laser — Beam expander

Dichroic beam splitter

Achromat lens

Pin hole

Computer

Photomultiplier detector

PHOTOELECTROCHEMICAL MICROSCOPY OF METALS

* Precursor Sites for Pitting
* Variation of Surface State Concentration over Local Oxide Regions

---

LOCAL REACTIVITY OF METAL SURFACES

* Relative Etching on Polycrystalline Surfaces
* Local Reaction Rates

3D MAPPING OF HETEROGENEOUS SURFACES

* Pore Mapping by Fluorescence Microscopy
* Optical Profilometry and Surface Roughness

The microscope schematic diagram features two focal points and scanning of the laser beam which discriminates against data that is not in the focal plane at the detector. Thus "optical slices" in the z direction may be assembled to make 3-D images of heterogeneous and rough materials.
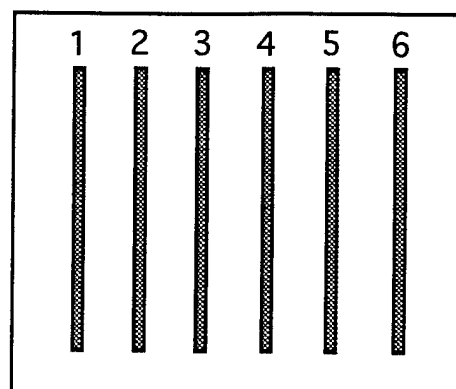
HOPG
Substrate

Figure 2

FLUORESCENT INDICATOR IN NAFION

1. FLUORESCEIN

2. RHODAMINE B

3. CRYSTAL VIOLET

4. OXAZINE 4

5. MALACHITE GREEN

6. RHODAMINE 6G

Figure 3. Fluorescence Microscopy Image of Two Dyes Deposted In Nafion on a HOPG Substrate

Figure 4.   The Research on PEMFC At The University of Minnesota Has Three
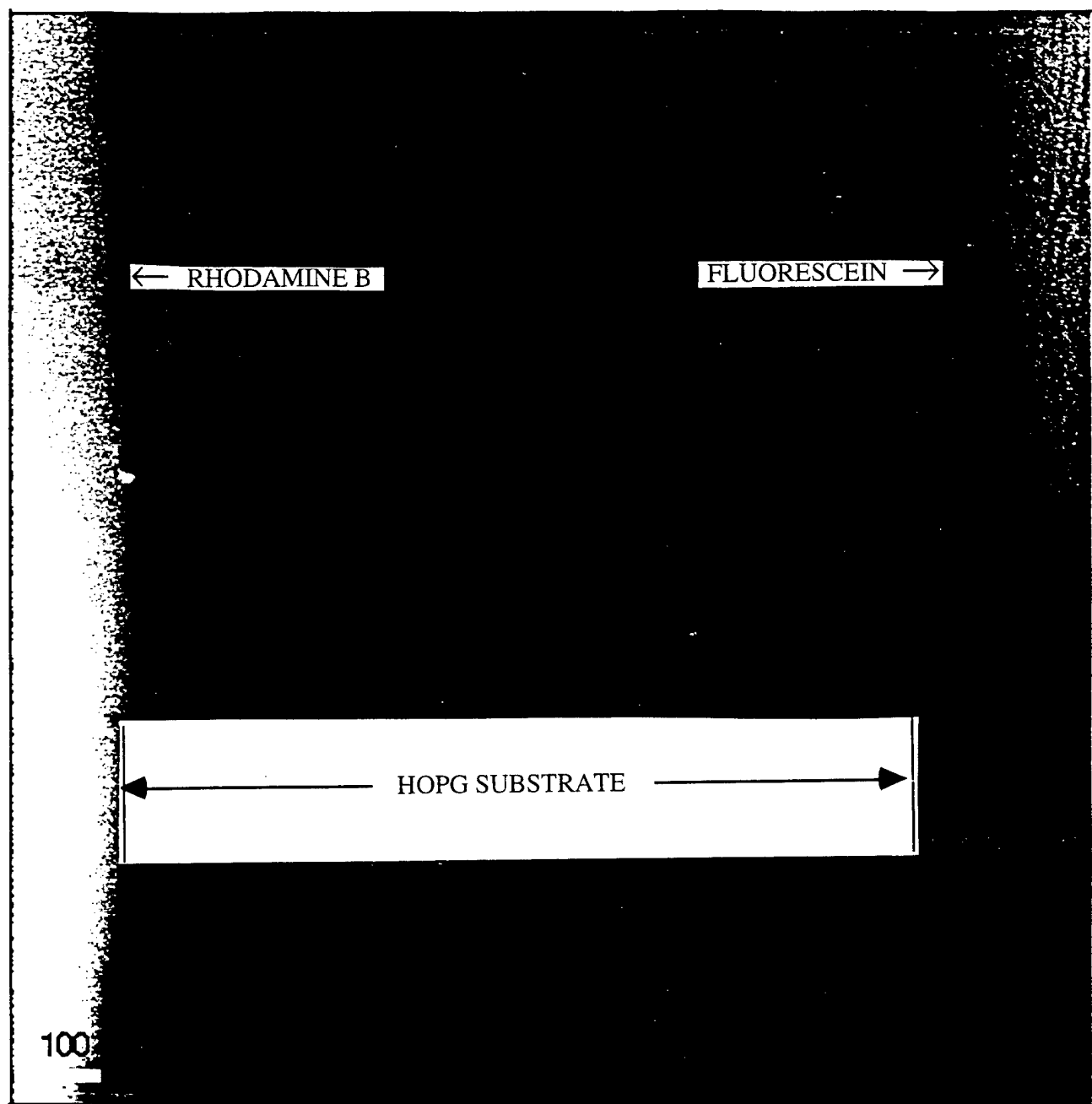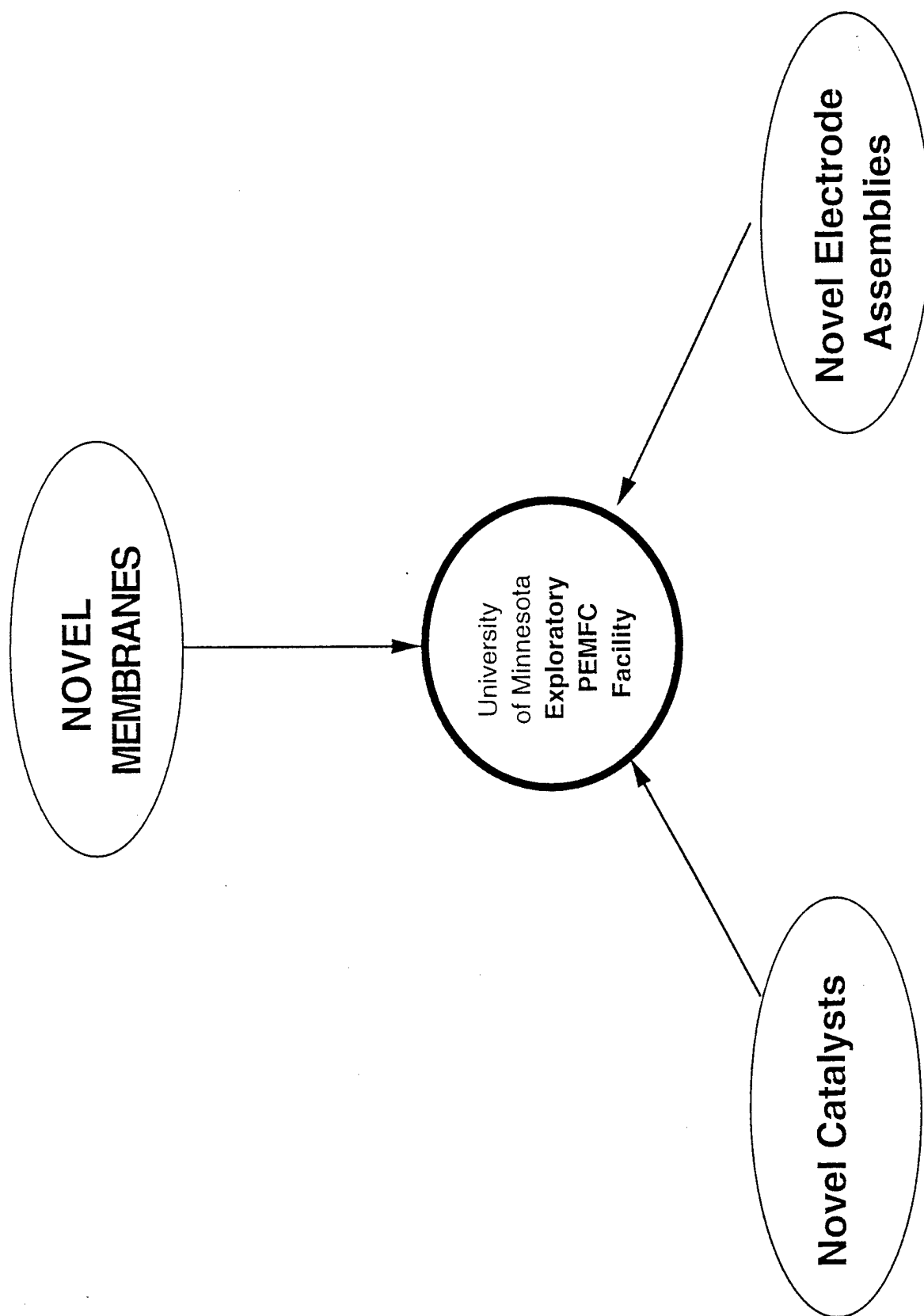Components That are Integrated By the Exploratory Facility

POLYMER ELECTROLYTE MEMBRANES FOR FUEL CELLS

Günther G. Scherer
Paul Scherrer Institut
General Energy Research
Electrochemistry
Ch-5232 Villigen PSI
Switzerland

In the past the development of Polymer Electrolyte Fuel Cells (PEFCs) has profited greatly from the availability of perfluorosulfonic acid membranes (DuPont (Nafion), Dow). These membranes show excellent stability in the harsh environment of a fuel cell and, therefore, allow the study of various aspects of fuel cells, e.g., electrocatalysis, membrane-electrode-interface preparation, design of flow fields for gas distribution, systems integration, and many others, without dealing with the problem of membrane degradation during operation of the respective experiment. However, the high price of these membranes today, in the range of $800 to 900/m^2, has contributed to the slow introduction of polymer electrolyte fuel cell technology in various areas. This is one of the reasons why in many laboratories research is going on to develop low-cost proton-conducting membranes for this fuel cell technology.

In this contribution a short overview is given about membrane development in various European laboratories. Many of these developments have started only recently and focus primarily on the low-cost aspect for fuel cell technology in transport applications. From these developments membranes for disposable fuel cell applications may energy spin-off.

Membranes Based on Fluorinated Polymers

Work concerns the preparation of proton-conducting membranes by radiation grafting selected monomer/crosslinker mixtures onto fluorinated trunk polymers and subsequent sulfonation of the grafted monomer (PSI, Switzerland; Morgane, France). Gamma, as well as electron irradiation, is utilized. This easy method of film modification offers the possibility to tailor membranes for a variety of applications. The stability of these membranes on the basis of styrene as graft component has still to be improved in order to have the lifetimes necessary for transport applications. However, current demonstrated lifetimes would be sufficient for disposable fuel cells.

Research at a very fundamental level is being carried out to study radiation grafting into capillary pore membranes, which are originally irradiated by heavy ions and subsequently track etched to develop capillary pores (CEA, France).

In contrast to the situation in the United States and in Japan, there is no publicly known development of advanced perfluoro sulfonic acid type membranes. However, work is going on to plasma deposit perfluorosulfonic acid films directly onto electrode structures (Fraunhofer Gesellschaft, Germany).

Membranes Based on Hydrocarbon Polymers

Chemically- and thermally-stable main-chain polyaryl-ether type polymers (Polysulfone (Univ. Freiburg and Stuttgart, Germany), Polyetherketone (Hoechst Ag, Germany), Polybenzimidazole (Univ. Montpellier, France), Polyimides (CEA, France), etc.) are believed to be excellent fluorine-free and potentially low cost candidates as base polymers. Sulfonation is easily carried out to render them to proton-conducting membranes. Solubility of these polymers in selected solvents opens the possibility of recycling used membranes.

Composite Membrane

Composite membranes based on an inorganic proton conductor and an organic polymer binder are being developed for application in Direct Methanol Fuel Cells (Innovision, Denmark; CEA and CNRS, France; Joule III Project, Italy, France, Germany). It is to be expected that methanol crossover can be drastically reduced in comparison to the perfluorosulfonic acid membranes. A major development problem is to over-come the low specific conductivities of the percolated inorganic proton conductor phase within the binder matrix.

A brief overview of the state of the art of these development routes will be presented. Unfortunately, for many of these developments only very preliminary fuel cell test results are available today. These results concern mainly the stability requirement and quite often other membrane properties, which are important for a fuel cell as a system, e.g., humidification and water management, are neglected at this development stage. Membrane development for this technology requires comprehensive polymer materials research focusing on all membrane properties important for this technology.

BALLARD

Generalized Formula for BAM3G
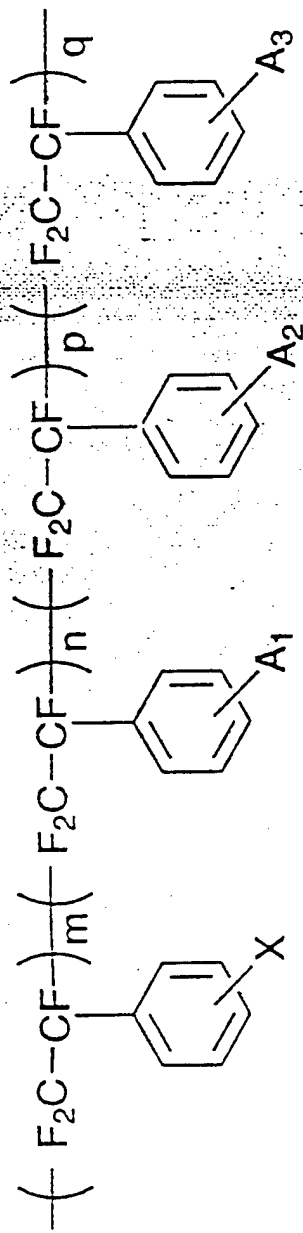
In the generalized formula, at least two of m, n, p and q are greater than zero, with X selected as SO_3H. The groups A_1, A_2, A_3 are selected from the series consisting of alkyl, perfluoroalkyl, halogen, etc.

Development of Cheap Proton Exchange Membranes
for Fuel Cells in Electric Vehicles

Plasma Deposition System with two Ion Beam Sources

R.F. Negative Ion Beam Source

Air Inlet

Recipient

Pumping System

G_1

G_2

O_2

H_2 SO_2

Target Holder

Substrate Holder

G_2

G_1

V

R.F. Positive Ion Beam Source

G_1, G_2 Acceleration Grids
V Acceleration Voltage

Fraunhofer Institut
Chemische Technologie
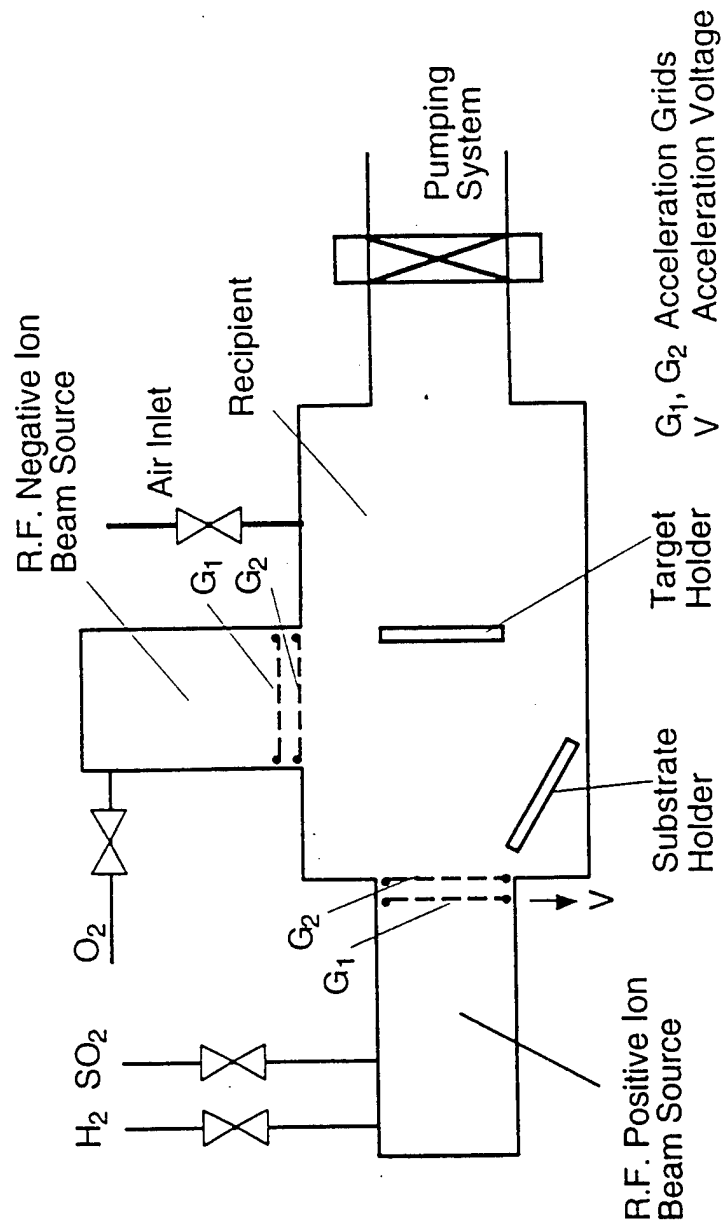
Stability of radiation-grafted membranes in a H$_2$/O$_2$ fuel cell.

Fuel cell conditions : 0.8 mg cm^{-2} Pt , T = 60°C

H$_2$/O$_2$, ambient pressure

N117

RAI 1010

PSI

RAI 4010

M$_1$

R [mΩ cm^2]

t [h]
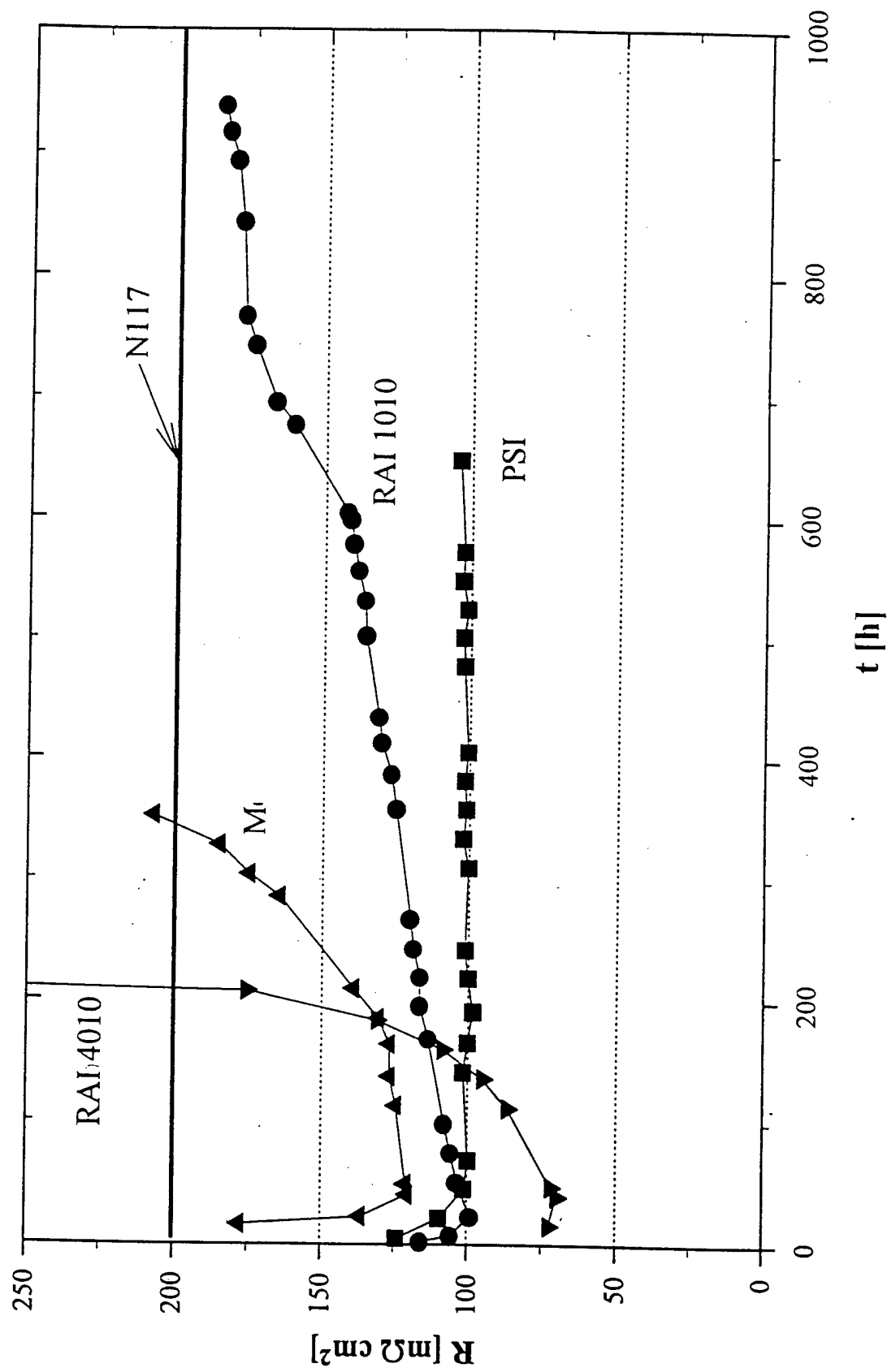
Maximum power density [f(t)].

$0.8 \text{ mg cm}^{-2} \text{ Pt.} \quad T = 60°C$
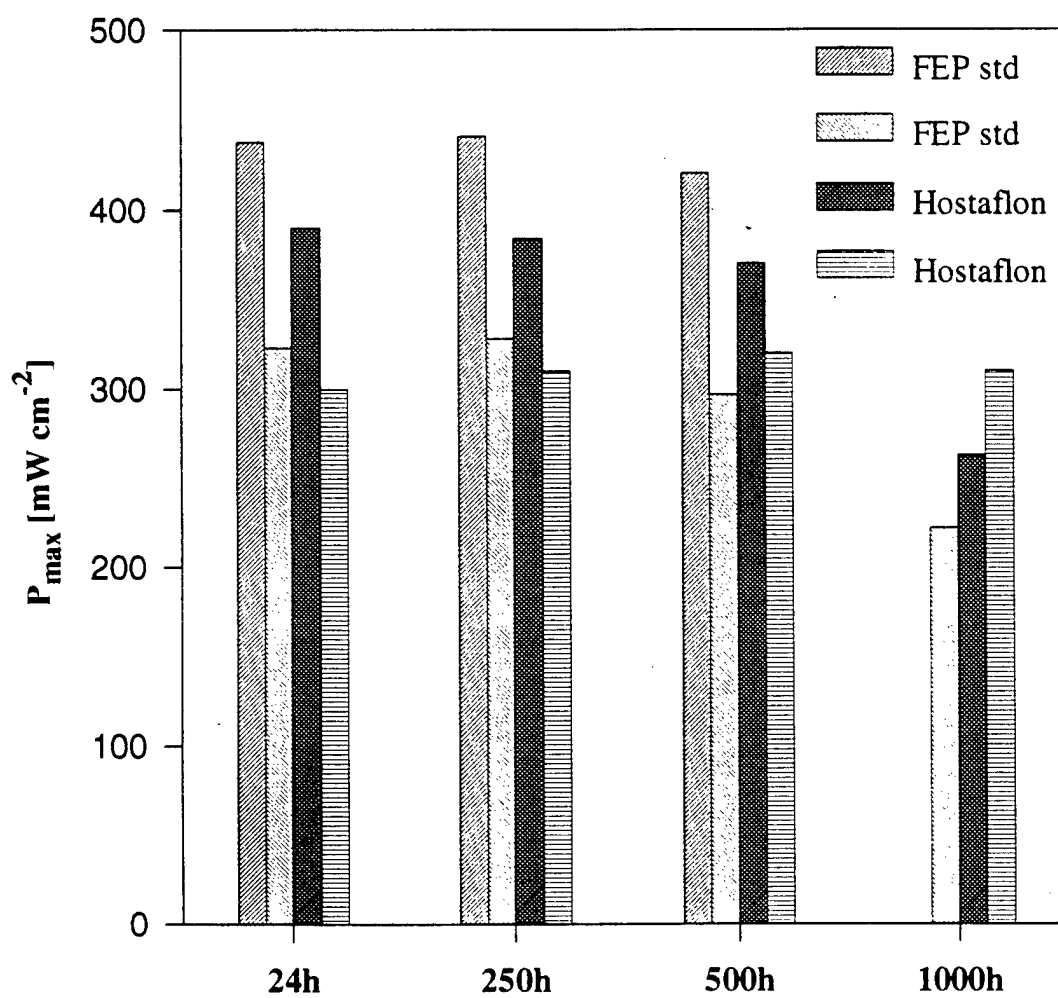
Sulfonated Polysulfone

1988	C. Arnold, Sandia Lab.
1993	C. Linkous, Florida Solar Energy Center
1993	K. Ledjeff, R. Mühlhaupt, Univ. Freiburg/Br.
1994	J. Kerres, Univ. Stuttgart
1994	Innovision, Denmark
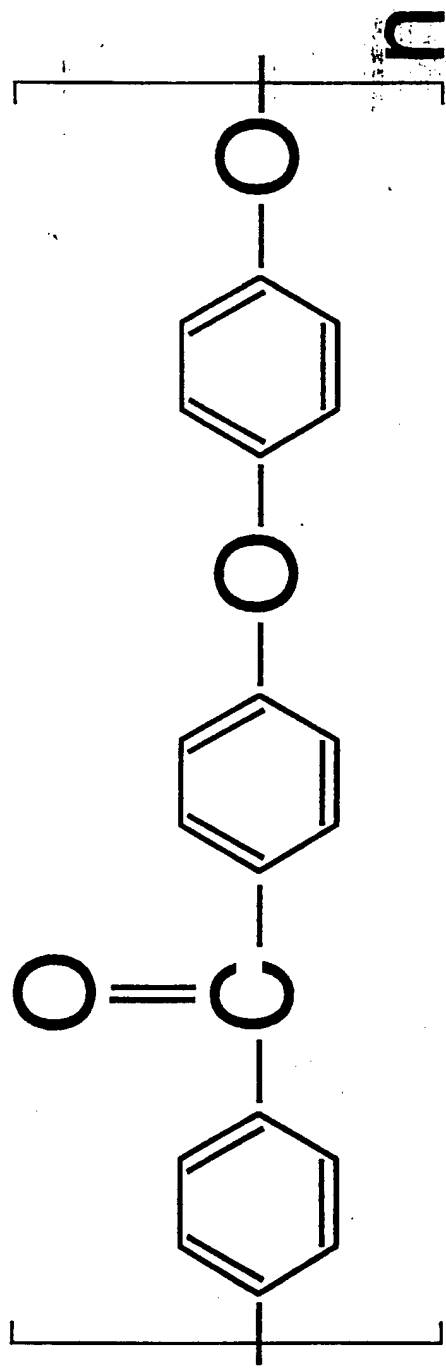
PEEK

Hoechst AG

POLYIMIDES

PAUL SCHERRER INSTITUT

(MDA)

(BDSA)

(ODPA)
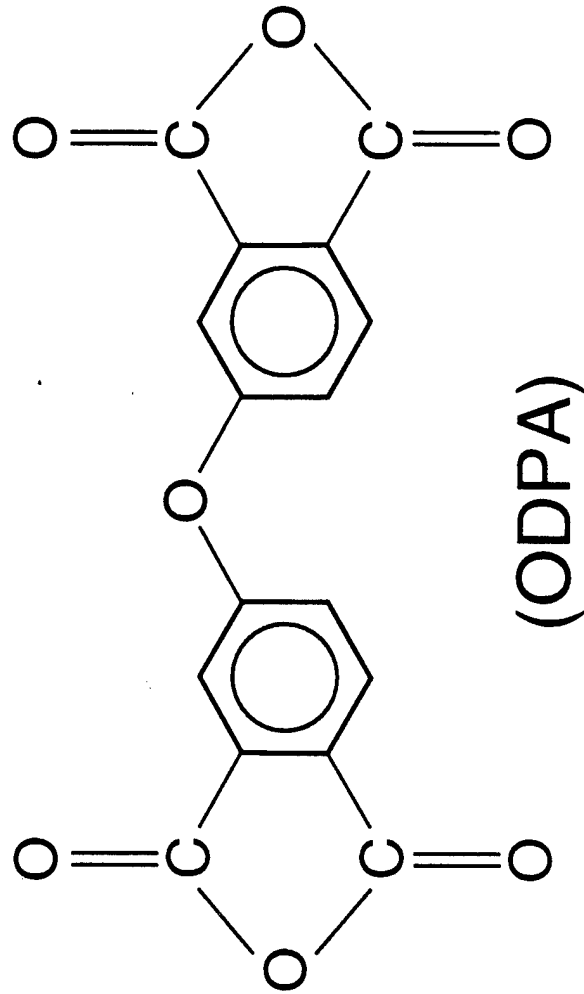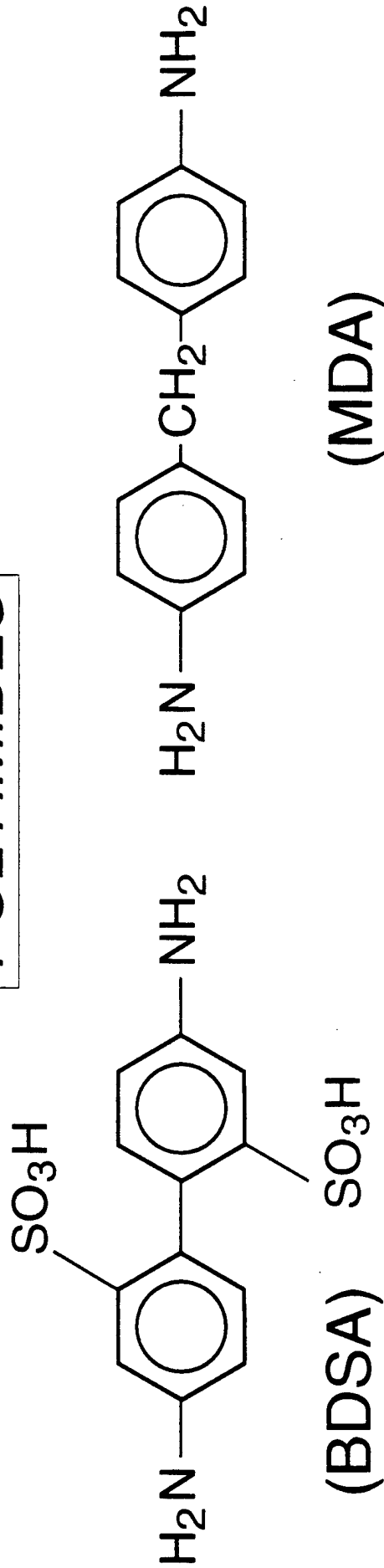
CEA Grenoble
Univ. Lyon
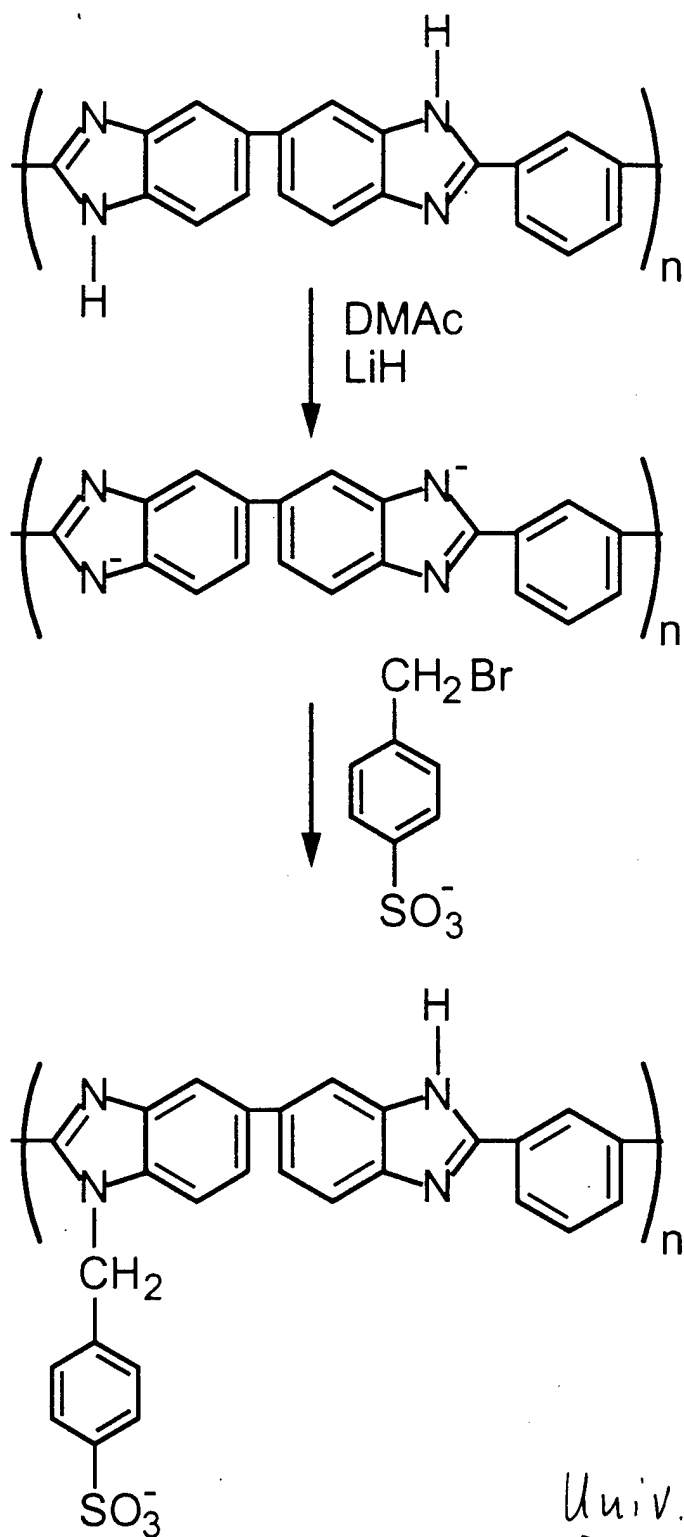
Synthesis of sulfonated polybenzimidazole:
grafting of bromomethylbenzenesulfonate

SG51-7/KI82

Composite Membranes

Solid State Superprotonic Conductor

Phosphatoantimonic Acid (H3)
$H_3Sb_3P_2O_{14}, xH_2O$ $\sigma(20\ ^\circ C, 100\ \%\ RH)$ $3\times10^{-2}\ Scm^{-1}$

Mordenite-Keggin Salt $\sigma(20\ ^\circ C, 100\ \%\ RH)$ $1\times10^{-2}\ Scm^{-1}$

$M(HPO_4), xH_2O\ (M=Sn, Sb)$ $\sigma(80\ ^\circ C, 100\ \%\ RH)$ $3\times10^{-2}\ Scm^{-1}$

Nafion (EW1100) $\sigma(20\ ^\circ C, 100\ \%\ RH)$ $3\times10^{-2}\ Scm^{-1}$

Thermostable Polymeric Binder

PVDF, EPDM, PS, PDMS
Good Electrochemical and Thermal Stability, low Gas Permeability

Composite Membrane

EPDM-65 % H3 (raw) $\sigma(80\ ^\circ C, 100\ \%\ RH)$ $0.2\times10^{-2}\ Scm^{-1}$

EPDM-65 % H3 (lyophylised) $\sigma(80\ ^\circ C, 100\ \%\ RH)$ $0.8\times10^{-2}\ Scm^{-1}$

NEW ORGANIC-INORGANIC POLYMERIC MEMBRANE FOR H2/02 AND DIRECT METHANOL FUEL CELL

B. Baradie, C. Poinsignon, J.Y. Sanchez, Y. Piffard[1]

Laboratoire d'Ionique et d'Electrochimie des Solides de Grenoble, CNRS-NPG Domaine Universitaire BP 75, F-38402 St. Martin d'Hères, FRANCE

1 Institut des Materiaux de Nantes-CNRS 4, rue de la Houssinière, F-44072 NANTES Cedex

E (mV) vs I (A/cm²) — membrane composite, Nafion117
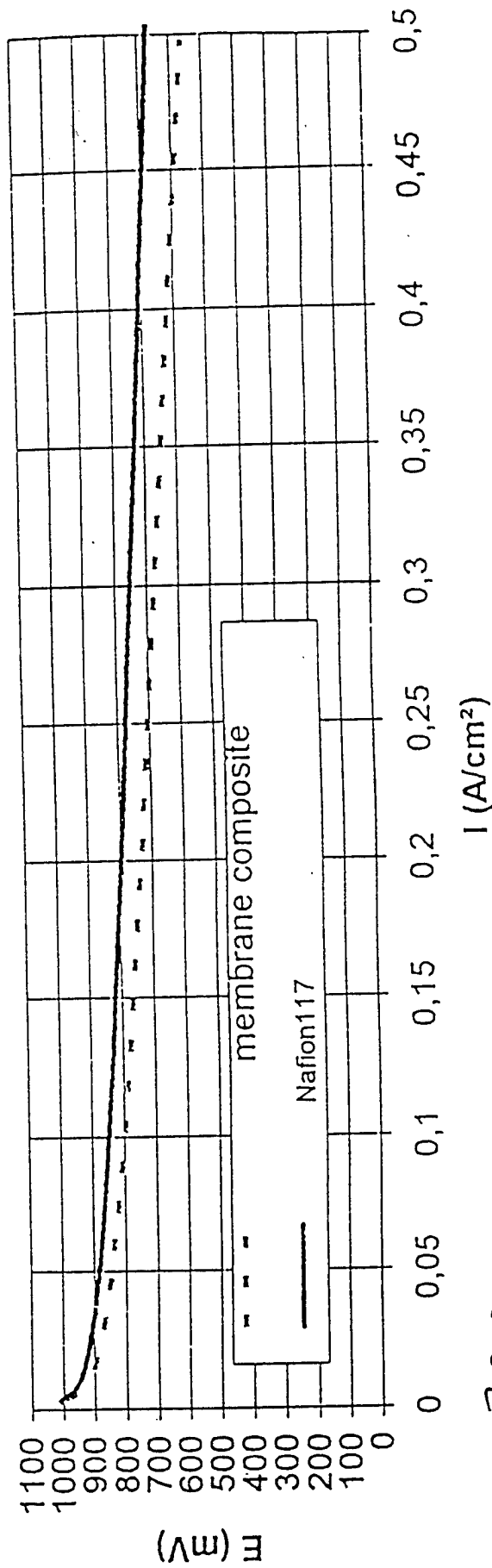
PORTABLE POWER FROM DISPOSABLE FUEL CELLS DIRECT METHANOL HIGH TEMPERATURE PEM AND ALUMINUM-OXYGEN

Robert F. Savinell

Ernest B. Yeager Center for Electrochemical Sciences
and Department of Chemical Engineering
Case Western Reserve University
Cleveland, OH 44106

PBI Direct Methanol Fuel Cells

A schematic of a direct methanol fuel cell is shown in Chart 1. Major challenges for this system include slow reaction kinetics at both the cathode and anode, fuel crossover, and for commercial and/or disposable applications, cost. There is a potential to address these challenges by utilizing proton conducting polymers capable of operating at elevated temperatures such as 200°C. This is the approach being taken at CWRU and Quad Chart 2 summarizes the objective, approach, and recent results of this program. Chart 3 presents some of the advantages and issues related to the high temperature fuel cell. The work at CWRU has identified a polymer system capable of conducting protons at elevated temperatures (200°C) and under atmospheric pressure conditions. The polymer, polybenzimidazole, is doped and phosphoric acid. The non-mobile acid conducts protons through presumably the Grotthus mechanism. The conductivity of this polymer can exceed that of Nafion under its optimally hydrated condition, and it provides a good barrier to the permeation of methanol. Chart 4 shows the structure of this polymer, its conductivity, and its permeation to gases. Membrane electrode assemblies (MEAs) have been fabricated and fuel cell performance demonstrated (see Quad Chart and Chart 5). At this time, the full benefit of the high temperature operation has not been realized. We feel that the electrode structures, a power density of about .3 W/cm^2 at 500 mA/cm^2. With improvements in electrode structures, a power density of about .3 W/cm^2 at this current density is not unreasonable. A twelve volt stack would require 20 to 24 cells and a 5 cm x 5 cm electrode area per cell will deliver about 100 watts of electrical power. Other issues challenging the development of pbi fuel cells are given in Chart 4 and work is currently underway to address these issues.

A significant issue for disposable fuel cells will be cost of materials. As shown in Chart 6, PBI could reduce the cost significantly as compared to the Nafion proton conductor (which does not conduct well at elevated temperatures and atmospheric pressure). Anode catalyst cost are also significant. Unfortunately, there are no anode catalysts that surpass the performance of Pt/Ru. The strategy in short term will have to be the reduction of catalyst loading by achieving better utilization. There may be an alternative to Pt as the oxygen reduction catalyst. Pyrolized macrocycles have been demonstrated to perform on par with Pt and as an additional benefit, they are not affected by the crossover of methanol. Some of the benefits and issues of the macrocycle catalysts are given in Chart 7.

Aluminum-Air Fuel Cells

The aluminum-air system is a hybrid between a battery (aluminum is contained within the stack) and a fuel cell (oxygen is taken from the ambient air). Aluminum is a high energy density material. As shown in Chart 8, the specific energy for aluminum is about 4500 Wh/kg as compared to 3000 Wh/kg for methanol, both of which neglect the mass of water necessary for the reactions. Aluminum has a considerably higher energy density (12,000 Wh/l compared to 2400 Wh/l for methanol) because of its mass density (2.7 Kg/l).
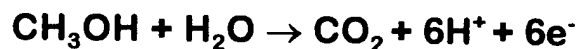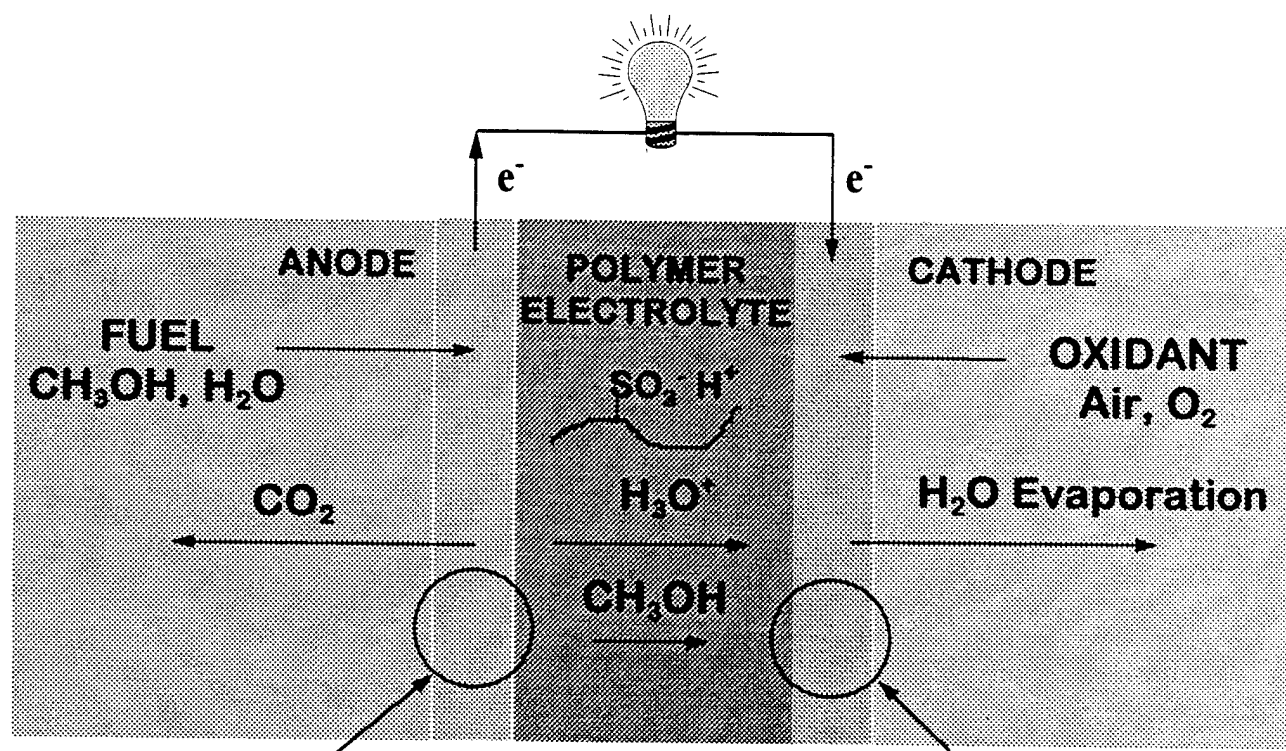
The reactions in the aluminum-air cell involves oxygen reduction in an alkali solution and aluminum oxidation to form aluminate ion. The hydroxide consumed in this reaction is restored in a separate crystalizer which precipitates aluminum oxide product. Although the theoretical potential

for this couple is about 2.7 volts, practical open circuit potential is around 1.5 volts and operating potential is excess of 1 volt at current densities even greater than 120 mA/cm^2. A comparison of batteries and fuel cell energy densities is shown in Chart 9. The aluminum-air battery represents a design without electrolyte pumping. The small aluminum-air fuel cell is represented in the conceptual design shown in Chart 10. This design will nominally weigh about 28 pounds and produce about 7 kWh of energy at a delivery rate of about 100 to 250 watts. An initial estimates to refuel the stack is $200-$450 per 7 kWh. Over a third of the weight of this system is electrolyte which may be reduced through optimization. Also, there is a potential to utilize water available in the field. Attention to design may offer opportunities to further reduce weight especially in the stack box and frame materials.

Chart 11 demonstrates a scenario of using the aluminum-air system as a field battery recharger. Mission endurance of rechargeable lithium batteries can be extended significantly by adding an aluminum-air recharger.

The aluminum-air fuel cell has potential for being a low cost fuel cell. There is no membrane or cell separator required. Cathode catalyst need not be precious metal based. The aluminum oxide product is relatively benign and the caustic electrolyte will not cause taxing material challenges. The fuel cell can be operated from a cold start and shelf-life can be extended indefinitely by storing dry. Of course, there are a number of issues and challenges needing attention before this system becomes viable for disposable field service. Some of these are stated Chart 12. Perhaps the most challenging of these are the need to reduce the water inventory and the complexity of design. In summary, the aluminum-air system has many positive features for a disposable fuel cell system and should be given some serious consideration in further system studies.

CHART 1

DIRECT METHANOL PEM FUEL CELL

ANODE — POLYMER ELECTROLYTE — CATHODE

FUEL CH_3OH, H_2O

$SO_4^- H^+$

OXIDANT Air, O_2

CO_2

H_3O^+

H_2O Evaporation

CH_3OH

$$CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^-$$

$$O_2 + 4H^+ + 4e^- \rightarrow 2\,H_2O$$

OVERALL REACTION

$$CH_3OH + 1.5O_2 \longrightarrow CO_2 + 2\,H_2O$$

CHALLENGES

- SLOW ANODE KINETICS
- FUEL CROSSOVER LOWER FUEL UTILIZATION AND CATHODE POTENTIAL
- MEMBRANE AND ELECTRODE COSTS

CHART 2

ARPA UNIVERSITY RESEARCH INITIATIVE

ADVANCED METHANOL-OXYGEN SOLID POLYMER ELECTROLYTE FUEL CELLS

CASE WESTERN RESERVE UNIVERSITY and CLEMSON UNIVERSITY

OBJECTIVES

- Develop ion conducting polymers for operation at 200°C for stable, high performance, light weight fuel cells.
- Develop and test catalysts and electrode structures for a MeOH-oxygen fuel cell using such polymers.
- Understand kinetics and mechanisms of methanol oxidation and oxygen reduction within a polymer environment at temperatures up to 200°C.
- Extend findings to lower temperature fuel cells.

ACCOMPLISHMENTS

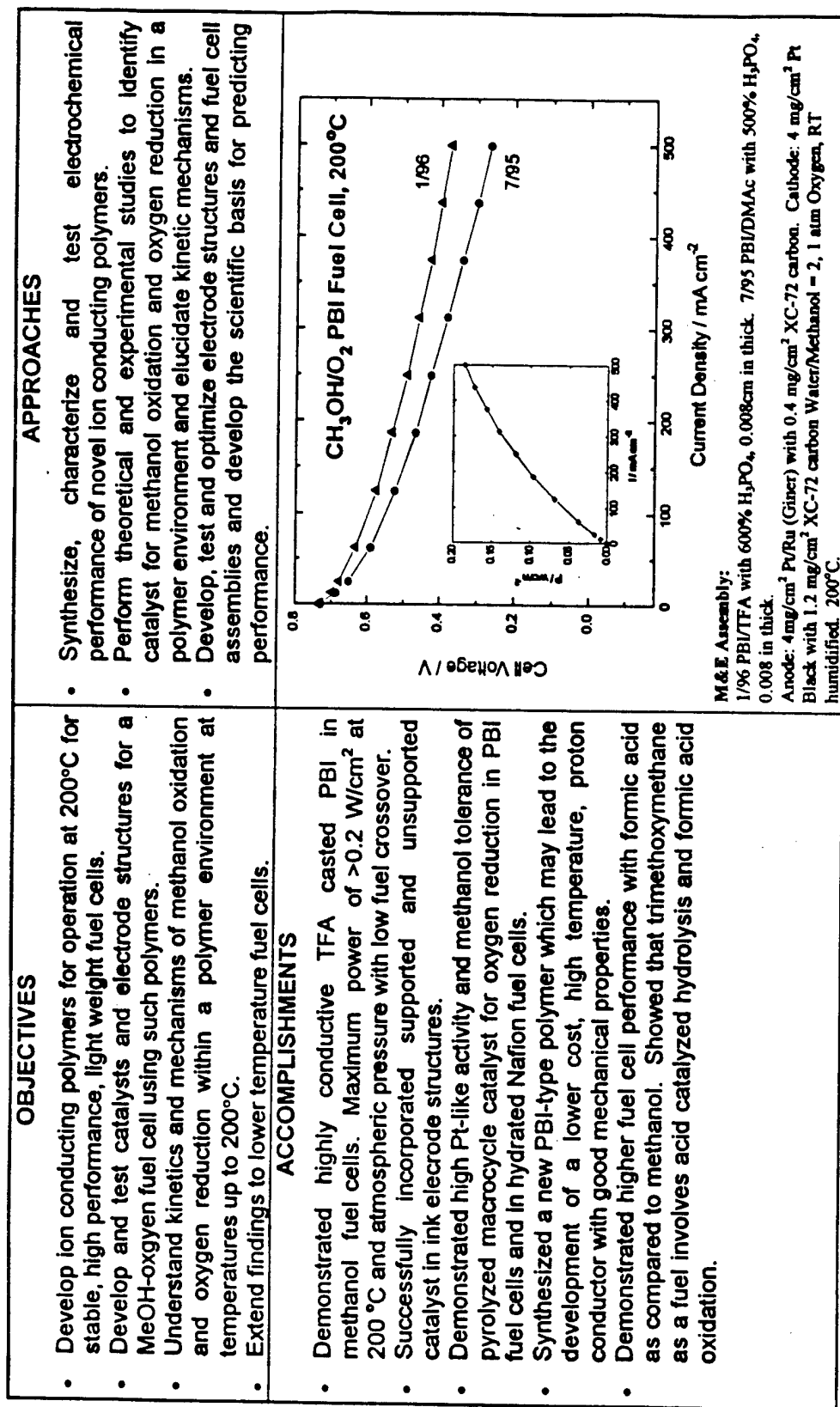- Demonstrated highly conductive TFA casted PBI in methanol fuel cells. Maximum power of >0.2 W/cm² at 200 °C and atmospheric pressure with low fuel crossover.
- Successfully incorporated supported and unsupported catalyst in ink elecrode structures.
- Demonstrated high Pt-like activity and methanol tolerance of pyrolyzed macrocyle catalyst for oxygen reduction in PBI fuel cells and in hydrated Nafion fuel cells.
- Synthesized a new PBI-type polymer which may lead to the development of a lower cost, high temperature, proton conductor with good mechanical properties.
- Demonstrated higher fuel cell performance with formic acid as compared to methanol. Showed that trimethoxymethane as a fuel involves acid catalyzed hydrolysis and formic acid oxidation.

APPROACHES

- Synthesize, characterize and test electrochemical performance of novel ion conducting polymers.
- Perform theoretical and experimental studies to identify catalyst for methanol oxidation and oxygen reduction in a polymer environment and elucidate kinetic mechanisms.
- Develop, test and optimize electrode structures and fuel cell assemblies and develop the scientific basis for predicting performance.

CH_3OH/O_2 PBI Fuel Cell, 200°C

M&E Assembly:
1/96 PBI/TFA with 600% H_3PO_4, 0.008cm in thick. 7/95 PBI/DMAc with 500% H_3PO_4, 0.008 in thick.
Anode: 4mg/cm² Pt/Ru (Giner) with 0.4 mg/cm² XC-72 carbon. Cathode: 4 mg/cm² Pt Black with 1.2 mg/cm² XC-72 carbon Water/Methanol = 2, 1 atm Oxygen, RT humidified. 200°C.

CHART 3

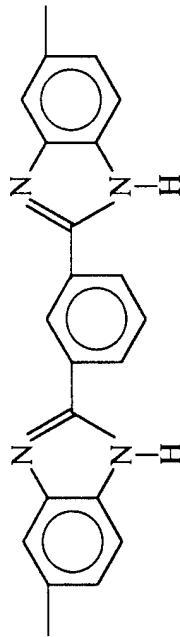# HIGH TEMPERATURE FUEL CELLS

ADVANTAGES

- Enhanced Electrode Kinetics

- Vapor Feed-Attitude Insensitive

- Low Crossover

- More Efficient Heat Transfer

ISSUES

- Design Needed For Rapid Start-Up

- Product Separation And Fuel Recycle

CWRU

CHART 4

PBI Membrane Electrolyte

PBI Repeat Unit

Conductivity of PBI membranes

Permeability of doped PBI (3-mil, DMAc cast)

Electrolyte	Gas	Temperature °C	Permeability
PBI/H3PO4	Methanol	150	270
Nafion 117	Methanol	80	80,000
PBI/H3PO4	Hydrogen	150	180
Nafion 117	Hydrogen	80	180
PBI/H3PO4	Oxygen	150	10
Nafion 117	Oxygen	80	90

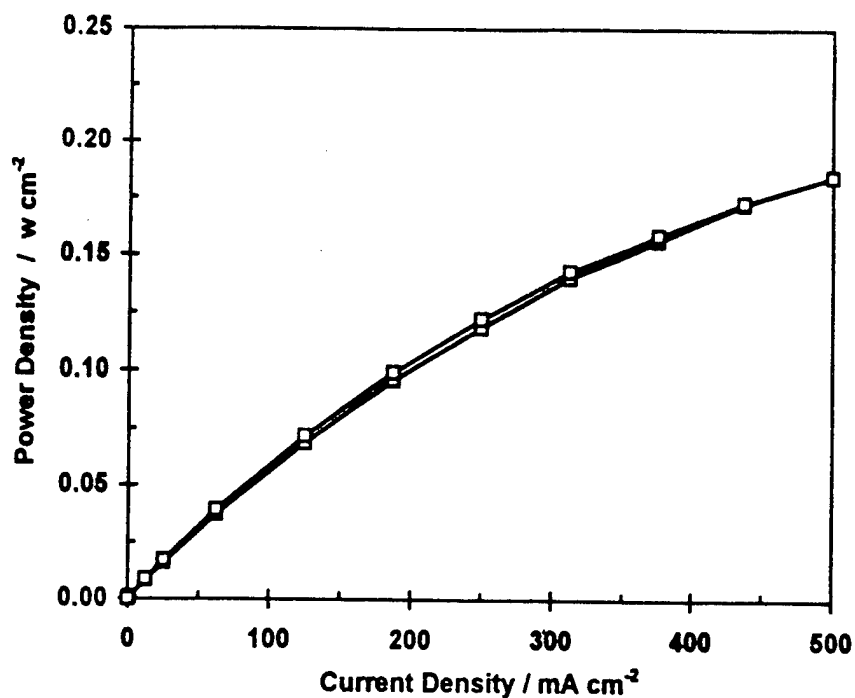Permeability Coefficients are given in barrer

1 barrer = $10\text{-}10$ cm^3(STP) cm / cm^2 s cmHg
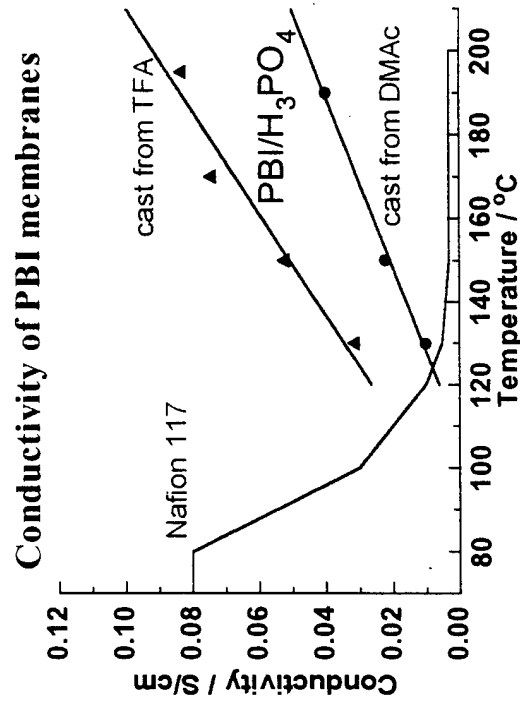
ISSUES

- Understand and Optimize Mechanical and Transport Properties
- Optimize Ionic Conductivity in Electrode Structures
- Realize Temperature Advantage on Reaction Kinetics
- Confirm Stability

CHART 5

PBI/TFA DMFC PERFORMANCE

T / °C	150°C	170°C	190°C	200°C
Cell Voltage / V at 500 mA/cm^2	0.250	0.288	0.336	0.370
Open Circuit Cell Voltage / V	0.630	0.663	0.700	0.719
Cathode Potential/V at 500 mA/cm^2	0.706	0.726	0.746	0.759
Anode Potential/V at 500 mA/cm^2	0.344	0.331	0.310	0.289
Cell Resistance / Ω	0.281	0.268	0.251	0.249

CHART 6

CWRU

DMFC MATERIALS

COMPONENT	MAT'L	LOADING	COST/KG	COST/KW*	ADVANTAGES	DISADVANTAGES
Separator	Nafion	7 mil	$2,200	$430	Commercial	T < 100°C High Crossover
	PBI	3 mil	$220	$18	High Temperature Low Crossover	T > 130°C Developmental
Anode	Pt/Ru	4 mg/cm^2	$10,000	$200	Commercial	Performance
Cathode	Pt	4 mg/cm^2	$13,000	$260	Commercial	Meth. Intolerant
	Macrocycle	5 mg/cm^2	C, H, O, N	?	Meth. Tolerant	Developmental

*Assumes 0.2 w/cm^2 performance

CHART 7

OXYGEN REDUCTION CATALYSTS

PYROLYZED MACROCYCLES FeTMPP, FeOEP

BENEFITS
- No Precious Metal Content
- Performance Rivals Pt
- Methanol Tolerant

ISSUES
- Thick Electrodes
- Stability

NON-PYROLYZED MACROCYCLES

BENEFITS
- Tailored Surfaces And Synthetic Control
- Performance By Design
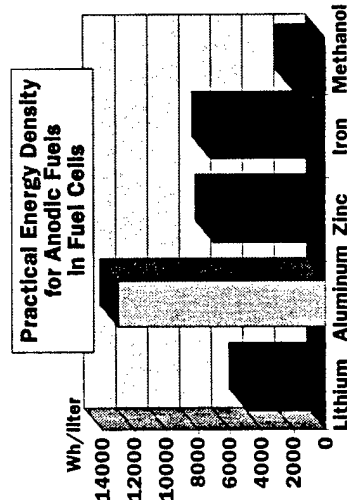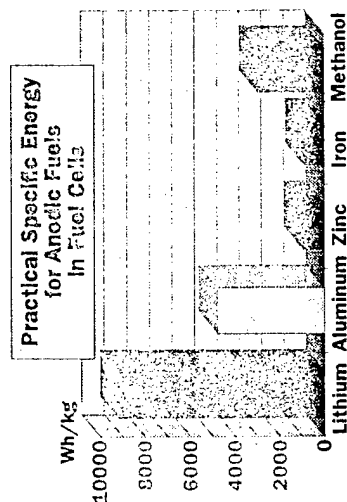
ISSUES
- Performance
- Stability
- Stability
- Stability

CWRU

CHART 8

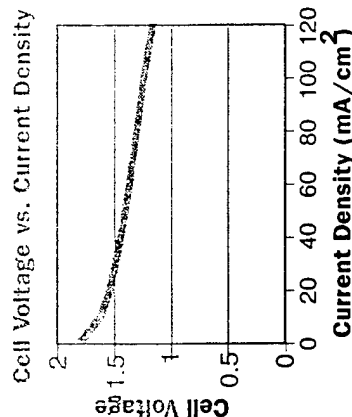# Aluminum Fuel Cell Technology

LORAL
Defense Systems-Akron

Aluminum Fuel Cells

Aluminum Fuel Cell with Electrolyte Management

Cell Stack

Air circulation

Cathode Reaction:
$3/4O_2+2/3H_2O+3e^- \rightarrow 3OH^-$

Anode Reaction:
$Al+4OH^-+K^+ \rightarrow KAl(OH)_4+3e^-$

Electrolyte circulation

Electrolyte Management

Crystallizer Reaction:
$KAl(OH)_4 \rightarrow KOH+1/2Al_2O_3 \cdot 3(H_2O)$

Cell Voltage vs. Current Density

Cell Voltage

0.5 1 1.5 2

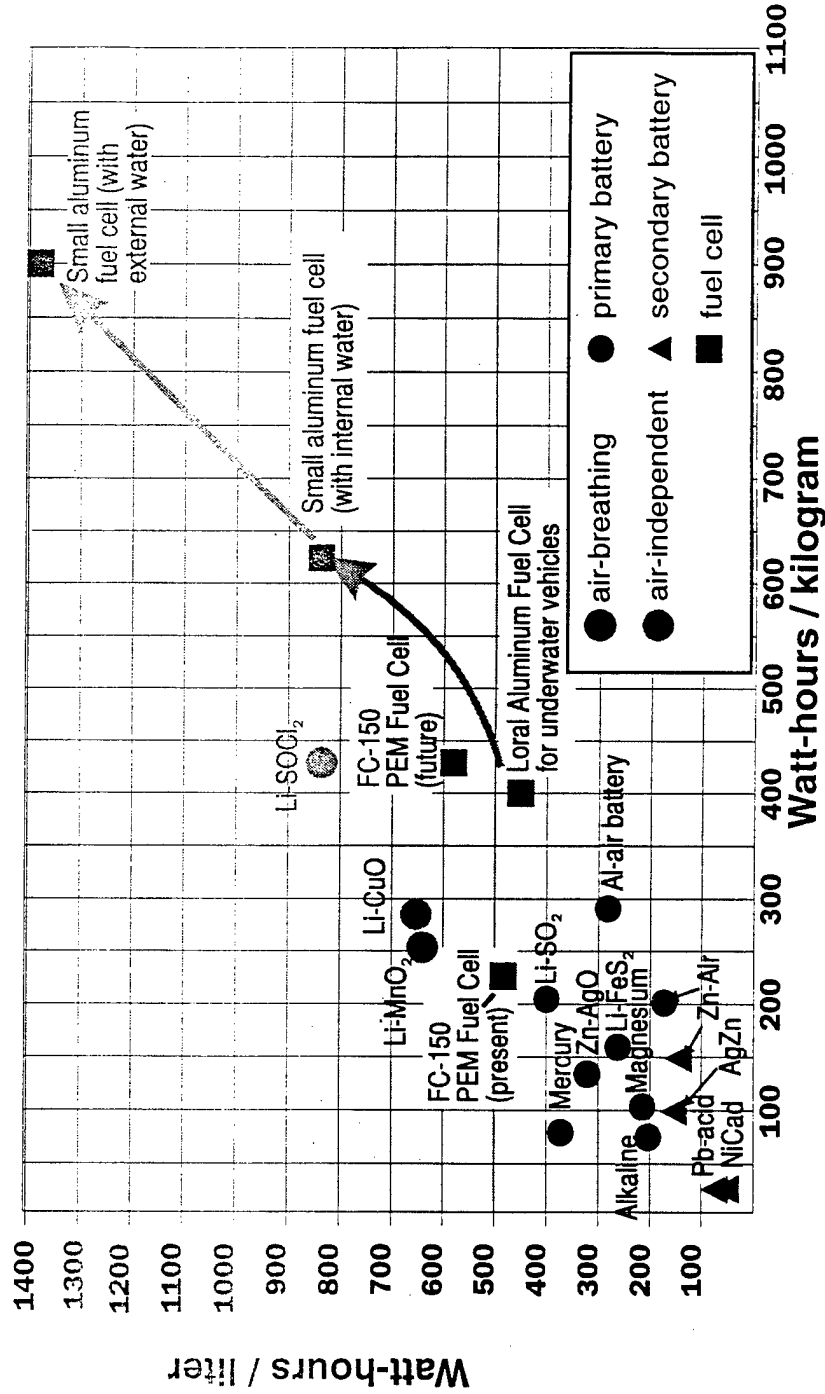Current Density (mA/cm^2)

0 20 40 60 80 100 120
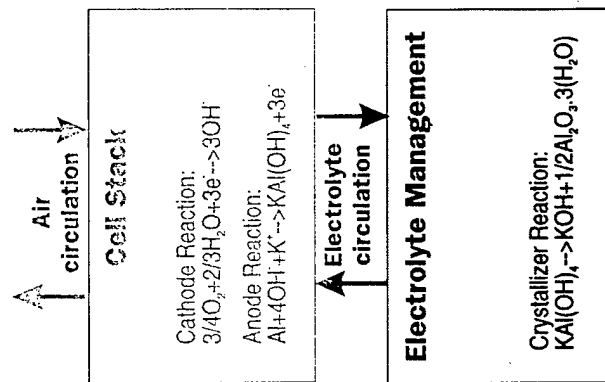
Aluminum's high energy potential has only recently become available due to the development of low corrosion aluminum alloys and high efficiency electrolyte management technology.

Aluminum Specific Energy & Energy Density

Practical Specific Energy for Anodic Fuels in Fuel Cells

Wh/kg

0 2000 4000 6000 8000 10000

Lithium Aluminum Zinc Iron Methanol

Practical Energy Density for Anodic Fuels in Fuel Cells

Wh/liter

0 2000 4000 6000 8000 10000 12000 14000

Lithium Aluminum Zinc Iron Methanol

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2 April 1996 s.l.sinsebaugh

CHART 9

LORAL
Defense Systems–Akron

Aluminum Fuel Cells

Comparison of Battery and
Aluminum Fuel Cell Technologies

Motivation: Aluminum power systems have the potential to provide
a significant increase in energy density over other technologies

Chart axes: Watt-hours / liter (vertical, 100–1400) vs Watt-hours / kilogram (horizontal, 100–1100)

Data labels: Small aluminum fuel cell (with external water); Small aluminum fuel cell (with internal water); Li-SOCl₂; FC-150 PEM Fuel Cell (future); Loral Aluminum Fuel Cell for underwater vehicles; Li-CuO; Al-air battery; Li-MnO₂; FC-150 PEM Fuel Cell (present); Li-SO₂; Mercury; Zn-AgO; Li-FeS₂; Magnesium; Zn-Air; Alkaline; AgZn; Pb-acid; NiCad

Legend:
- ● air-breathing, ● primary battery
- ● air-independent, ▲ secondary battery
- ■ fuel cell

\smallfc\vugraph2\sav-1.cdr
27 March 1996 s.l.sinsabaugh

CHART 10

LORAL
Defense Systems–Akron

Aluminum Power Systems:
Small Air-Breathing Systems

Aluminum
Fuel Cells

- This represents one possible configuration - others are possible for specific applications

- This system provides up to 7 kWh in energy and weighs about 28 lbs.

  - 7 kWh of LiSO$_2$would weigh over 77 lbs.
  - 7 kWh of NiCd would weigh over 600 lbs.

- Initial refuel cost estimates are in the range of $200 - $450 per refuel (7kWh)
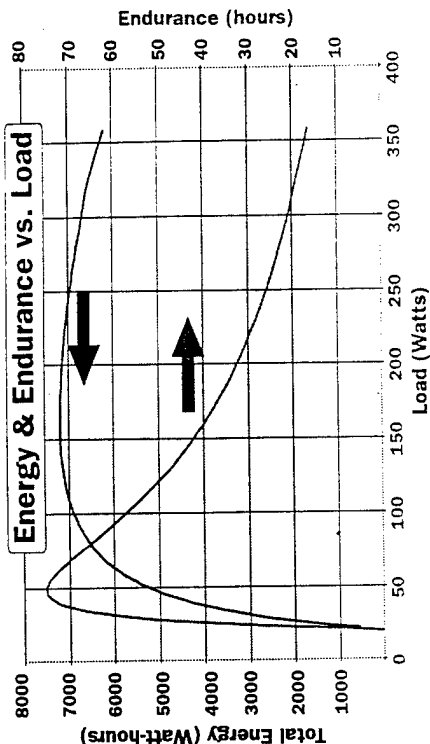
Cell Stack - 22 cells in series. Field replaceable for recharge.

Equipment Compartment - contains electrolyte pump, electrical controls, etc.

Energy & Endurance vs. Load

Endurance (hours)

Total Energy (Watt-hours)

Load (Watts)
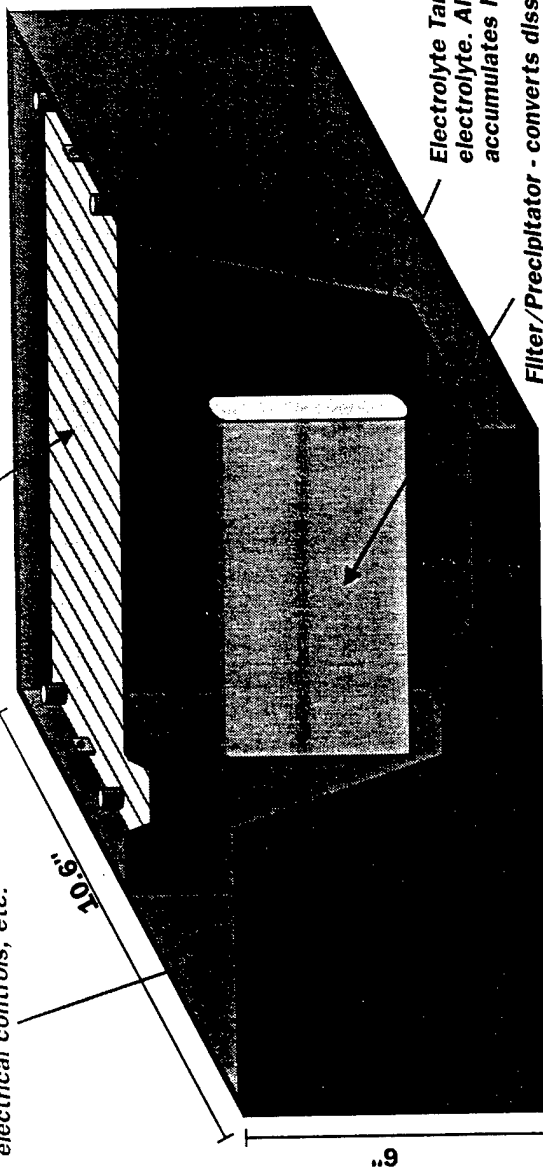
Component Weights (lbs)	
Aluminum Anodes	4.18
Cathodes	1.90
Frame Material	3.00
Miscellaneous Cell Parts	0.50
Electrolyte	9.77
Filter	0.50
Pump	1.00
Blower	1.00
Controls/Wiring	0.50
Box	4.87
Valve	0.50
SUM:	27.72

Electrolyte Tank - stores 2.2 liters of electrolyte. Aluminum byproduct accumulates here during discharge.

Filter/Precipitator - converts dissolved aluminum into a slurry that settles in tank, and regenerates electrolyte for stack
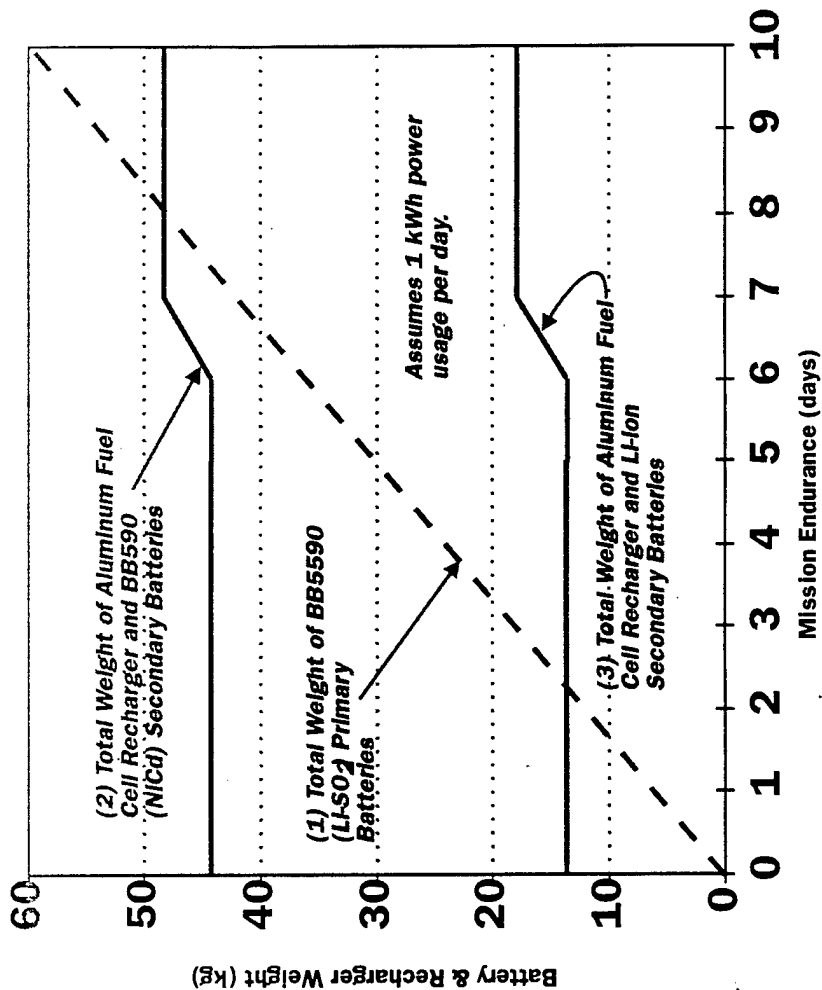
13.5"

10.6"

6"

.\smallfc\vugraph2\sav-2.ck
2 April 1996 s.l.sinsabaugh

CHART 11

LORAL
Defense Systems–Akron

Aluminum Fuel Cells

Soldier's Weight Load vs. Power Source

● A significant weight reduction for dismounted infantry is possible by replacing currently used primary batteries with secondary batteries and an aluminum fuel cell battery charger.

Battery & Recharger Weight (kg)

Mission Endurance (days)

(1) Total Weight of BB5590 (Li-SO₂) Primary Batteries

(2) Total Weight of Aluminum Fuel Cell Recharger and BB590 (NiCd) Secondary Batteries

(3) Total Weight of Aluminum Fuel Cell Recharger and Li-Ion Secondary Batteries

Assumes 1 kWh power usage per day.

\smallffc\vugraph2\sav-3.cdr
27 March 1996 s.l.sinsabaugh

CHART 12

ALUMINUM-AIR FUEL CELLS

ISSUES

MATERIALS

- Cathode Structure And Catalyst Costs

- CO_2 Tolerance Of Electrolyte

- Need Life Demonstration

- Anode Alloy Performance And Costs

- Disposing Aluminum Oxide Products

SYSTEM INTEGRATION

- Simplify Design

- Temperature Range For Operation

- Orientation Dependent Operation

- Rapid Recharge Design

- Voltage Variable With Time

- Water Management

- Hydrogen Management

- Need Low Power Pumps and Blowers

CWRU

DISPOSABLE FUEL CELLS.
PRELIMINARY THOUGHTS ON THE MAJOR CHALLENGES

Charles W. Martin
Clemson University
Department of Chemistry
Box 341905
Clemson, SC 29634-1905

Before presenting my thought on the problem at hand, let me first give the assumptions on which they are based. I am assuming that the disposable fuel cell in question will have to operate at a relatively low temperature ($< 60°$ C) with modest current densities (< 0.5 a/cm^2) and pressure (< 15 psig). Also, my main area of expertise is in the membrane end of the system so my discussion will be weighted toward that background.

It appears to me that there are two fundamentally different sets of challenges for those trying to develop a disposable, portable fuel cell. Those differences follow from the selection of the target fuel-hydrogen gas or methanol (or similar) liquid. The fuel to a great extent defines the areas in which new or improved technology is needed.

If hydrogen is the target fuel, the available membrane and electrode technology is quite good and the options are many. For a cell operating at low current density and below $60°$ C, even sulfonated polystyrene has lifetimes in the hundreds of hours. Membranes based on hydrocarbon ion containing polymers such as the new sulfonated polystyrene block copolymers offered by DAIS Corp. should be quite adequate in terms of lifetime and resistivity. This polymer is potentially very cheap compared to the fluorinated polymers such as Nafion if the market demand is reasonably large. The size of that demand, however, will probably depend on markets other than fuel cells. Lifetimes for hydrocarbon based membranes like these in the larger volume fuel cell applications such as transportation and stationary power are projected to be marginal to totally inadequate based on experience with sulfonated polystyrene. One interesting question that remains to be answered is how the internal reinforcement technology being developed by W.L. Gore and Associates will affect the useful lifetime of hydrocarbon based membranes. Gore is offering a membrane based on the DAIS polymer with or without electrodes.

On the other hand, the drive toward thinner, reinforced membranes has the potential to reduce the raw material cost of even fluorocarbon ionomer membranes dramatically. With the major research effort in MEA technology being focused on the chemically and thermally robust membrane materials, one must question the value of spending much effort on alternate membranes for a small volume application. Also, the fluorocarbon membranes should have unlimited shelf life. Hydrated, sulfonated polystyrene will support the growth of mold so biodegradation may be a problem for these and other hydrocarbon based polymers.

The bottom line is that the membrane will not be a basic problem for hydrogen based devices. Nor is the identity or cost of the catalyst a problem. The new technologies for low platinum loading MEAs (< 0.1 mg/cm^2) make the cost of the catalyst quite reasonable for the small electrode areas involved.

Beyond the MEA, there will certainly be many materials, design and engineering challenges to be overcome in packaging that MEA in a device that will produce power. However, my guess (possibly based on blissful ignorance) is that these are solvable. I think the biggest challenge in the design of a hydrogen powered device of this type is in storage and controlled delivery of the fuel. The reversible metal hydrides would be unacceptable in a disposable unit. High pressure hydrogen may be a possibility, but design of a safe, reliable, light weight, disposable container that is totally

impervious to hydrogen is a significant challenges as is the associated controlled delivery system. The chemical sources such as reactive metal hydrides plus water are a compact source but the reaction is highly exothermic and difficult to control. My colleagues in a proposed Engineering Center at USC are working on various approaches to this problem.

If methanol is the target fuel, one faces a different set of challenges. These include membrane permeability to methanol and slow kinetics with current electrode materials. The fundamental membrane problem is due to the high hydration in current ionomer membranes. In general, the hydration is required for effective proton transport. The low equivalent weight membranes that are most conductive also have the highest hydration. The more water in the membrane the faster the methanol transport to the cathode with the resulting loss in efficiency.

In our work at Clemson, we are addressing the problem by working to alter the relationship between hydration and conductivity. The hydration benefits conductivity in two ways. It provides the conductive medium for proton transport, and it increases the volume of the ionic cluster phase and thus increases the connectivity - the pathways for conduction through the insulating fluorocarbon matrix. As one increases the ionic content of a polymer, the osmotic swelling forces increase while the crystallinity that restrains that swelling decreases. If one could increase ionic content without a corresponding increase in hydration, one could potentially achieve high conductivity while minimizing hydration with a resulting decrease in methanol crossover.

We are evaluating two approaches. We have developed new thermoset perfluoropolymer technology that can potentially compensate for the loss in crystallinity and provide the restraint of swelling needed to reduce hydration. The crosslink occurs via a thermal dimerization which produces a perfluorocyclobutane linkage. Thus, the crosslink system does not introduce a reactive hydrocarbon site that would degrade in a strongly oxidizing atmosphere.

The second approach is to introduce novel strong acid functional groups such as perfluorosulfonimides that can be manipulated to modify hydration characteristics. Bisperfluorobutane sulfonimide is the strongest acid ever measured in the gas phase, i.e., in the absence of a protic solvent. The specific conductivity of the lithium salt of bis-trifluoromethyl sulfoimide is several fold higher than the corresponding lithium trifluoromethane sulfonate. Other novel ionic structures have also been incorporated into the perflurocarbon polymers for evaluation.

H$_2$ FUEL

No Fundamental Limitations from Membranes

Hydrocarbon Base ok if < 60°C < 0.5 a/cm^2 (?)

- Biofouling a Concern

- DAIS Corp.

Internally Reinforced Fluorosulfonic Potentially Low Cost

- Are HC Membranes Worth Pursuing?

Research Needs

- Will be Based on System Integration Issues

METHANOL FUEL

Membrane/Electrode the Limiting Technology

- Fuel Cross Over

- Electrode Kinetics

Membranes

- Crossover $\propto$ Hydration

- Hydration $\propto$ Conductivity

$\therefore$ Need to Change Conductivity Hydration Relationship

STRUCTURE OF
MONOMERS AND POLYMERS

* COPOLYMERS OF TETRAFLUOROETHYLENE

$$CF_2=CF_2$$

* WITH FUNCTIONAL VINYL ETHER MONOMERS

$$CF_2=CF$$
$$O(CF_2CFO)_n-CF_2CF_2SO_2F$$
$$CF_3$$

* $n = 1$ Long Side Chain (LSC)
* $n = 0$ Short Side Chain (SSC)

IONIC CONDUCTIVITY IN 5.5% HCL
DOW AND NAFION POLYMERS
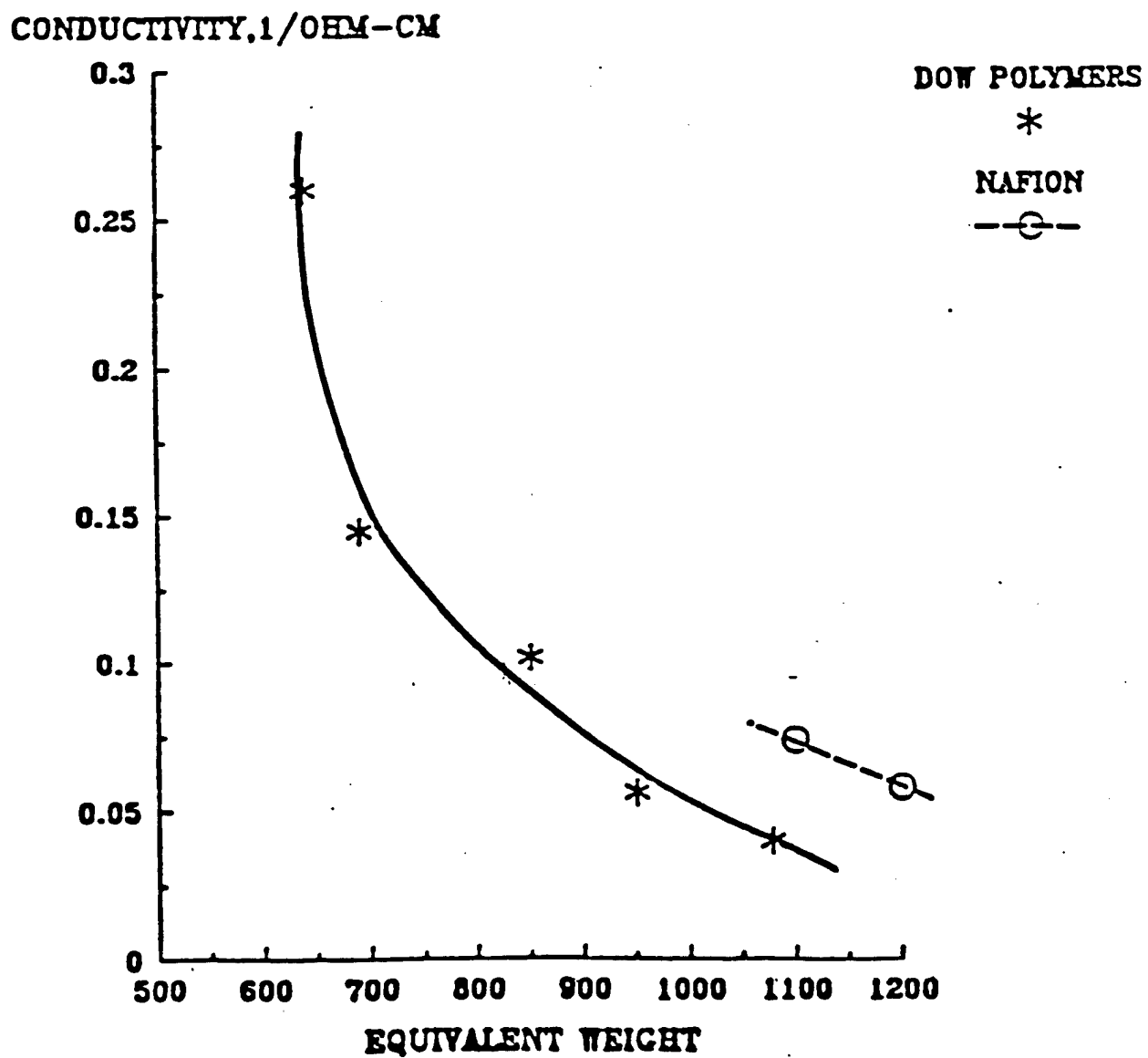
WATER ABSORPTION OF FLUOROPOLYMERS
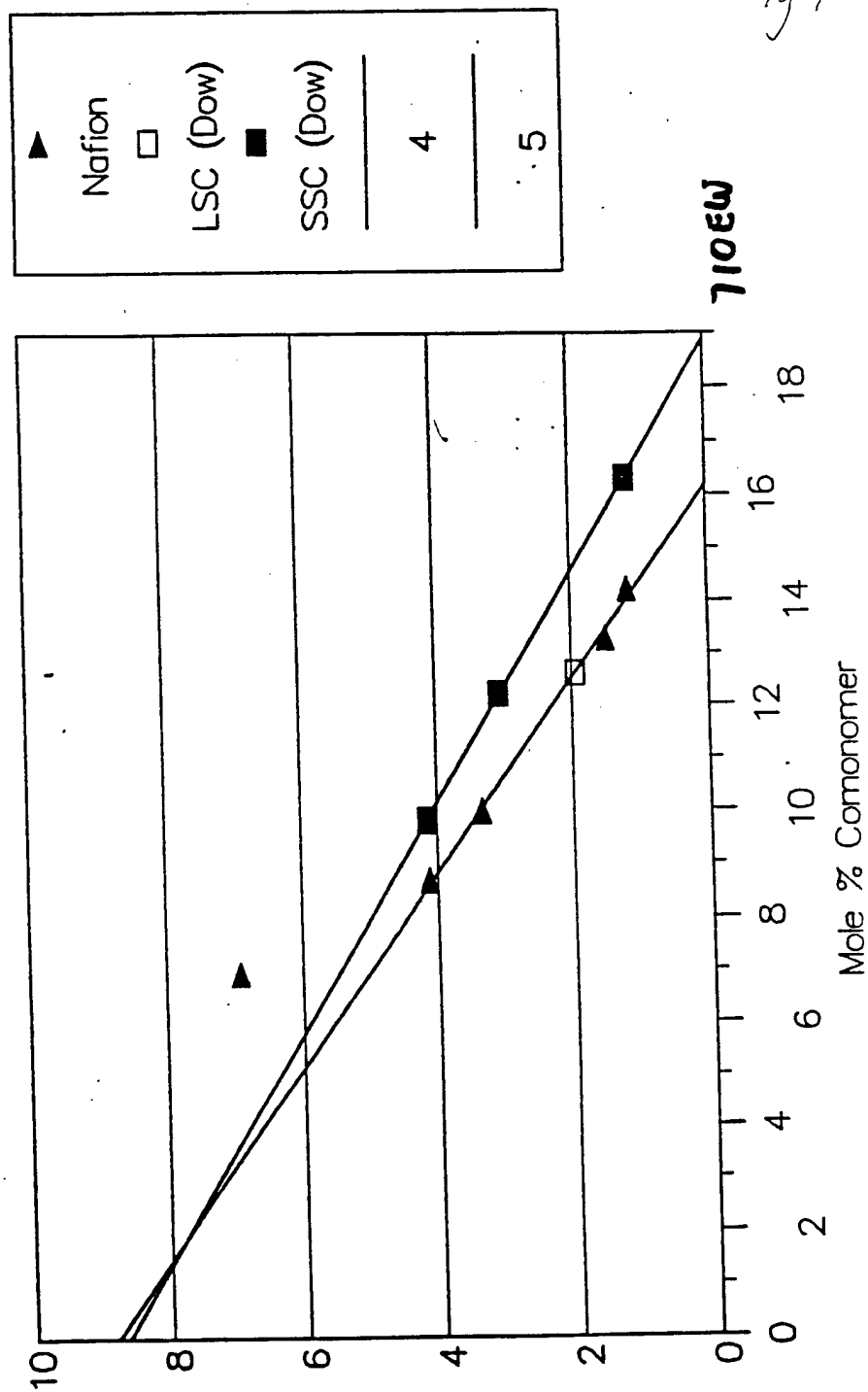VS EQUIVALENT WEIGHT

BC 9/90
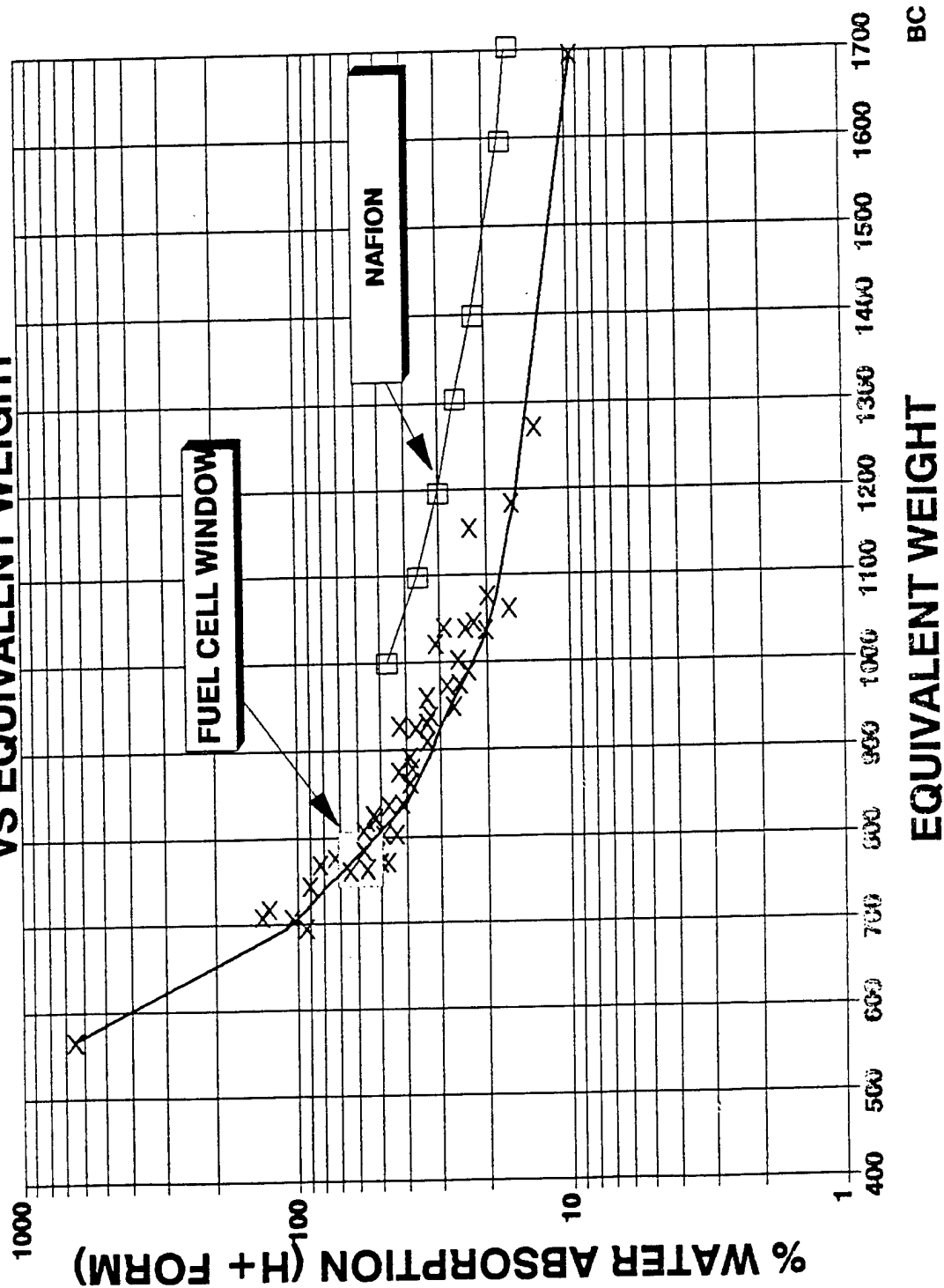
HYDRATION/FUNCTIONAL GROUP
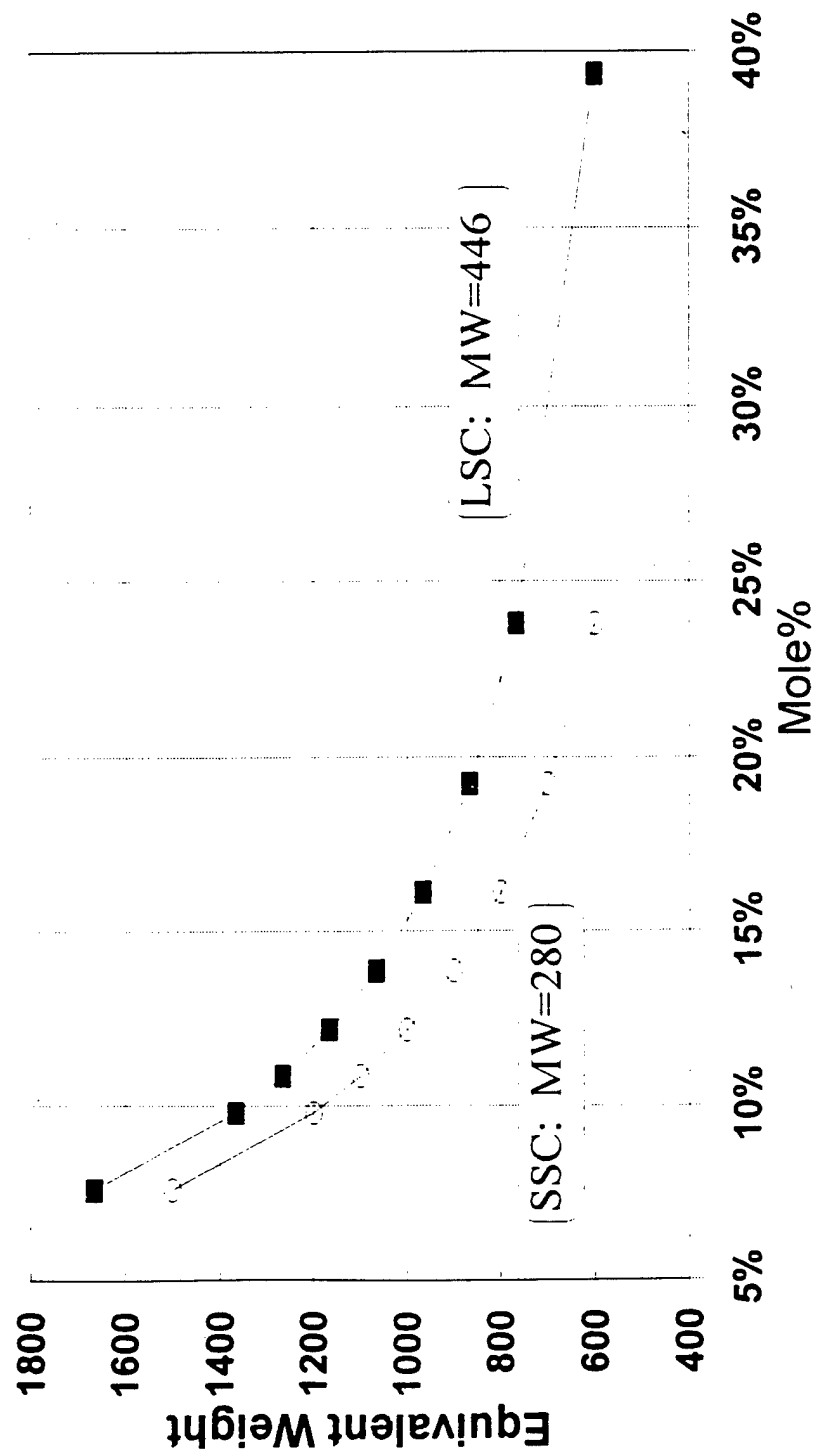## PERFLUORINATED SULFONIC IONOMERS
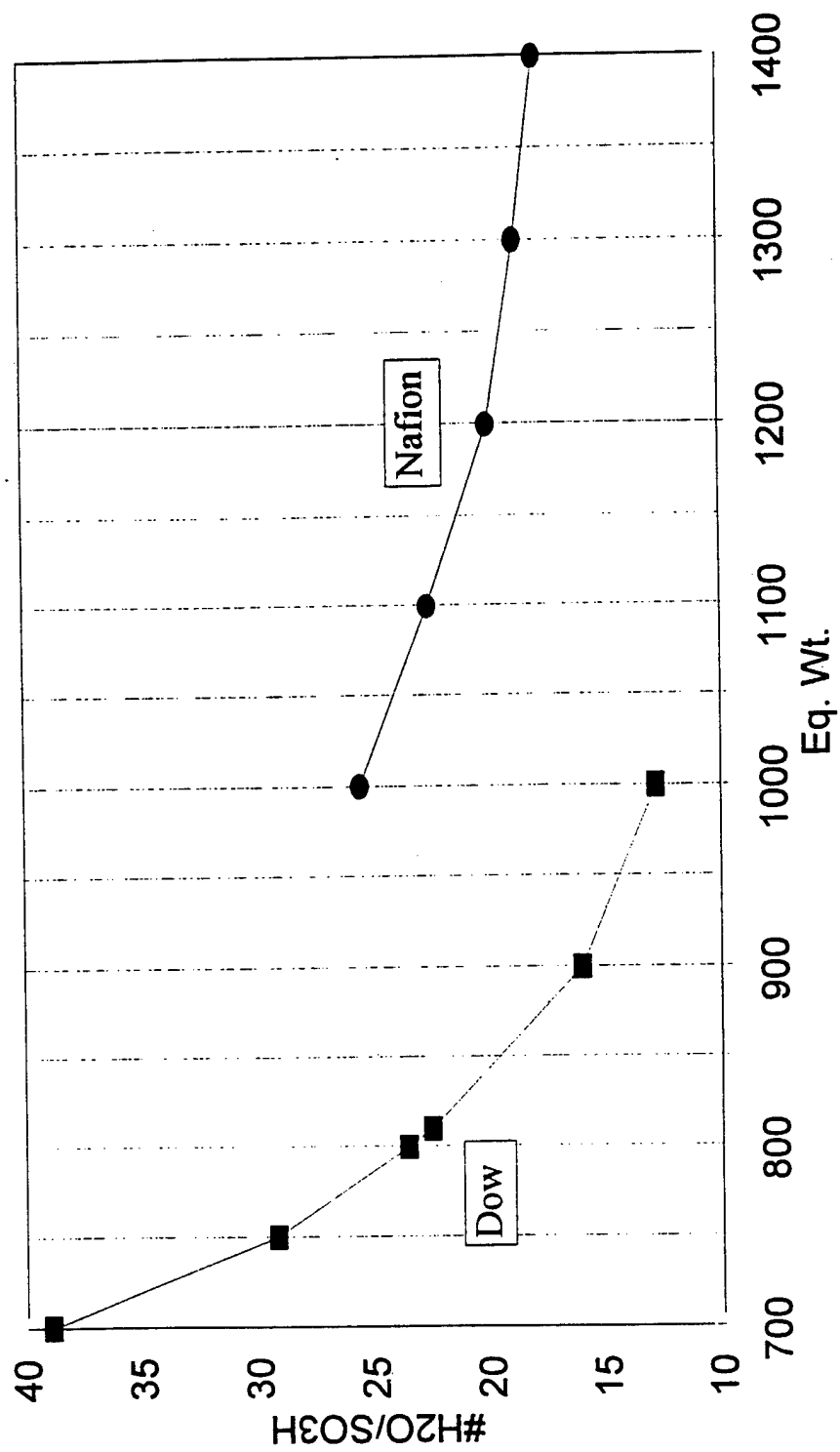
Crystallinity of LSC and SSC Sulfonic Polymers

Eq. Wt.	Mole%	% Crystallinity		
		-SO$_2$F	-SO$_3$Na	-SO$_3$H
SSC				
800	16.13%	7%	<2%	<2%
1000	12.20%	17%	7%	9%
1200	9.80%	24%	11%	13%
LSC				
1140	12.59%	8%	<2%	<2%

HEAT OF FUSION vs

MOLE % COMONOMER

Legend:
- ▲ Nafion
- ☐ LSC (Dow)
- ■ SSC (Dow)
- —— 4
- —— 5

x-axis: Mole % Comonomer

y-axis: ΔH (cal/g)

Mole % Comonomer vs. Equivalent Weight
Effect of Side Chain Length

GENERAL PFSA MICROSTRUCTURE

WAXS

Cluster Group

$-CF_2-CF_2-CF_2-CF_2-$

$-CF_2-CF_2-CF_2-CF_2-$

5 Å

SAXS

5 nm

1.5 nm

Fluorocarbon

Ionic Cluster

M. HEANEY 3/7/91
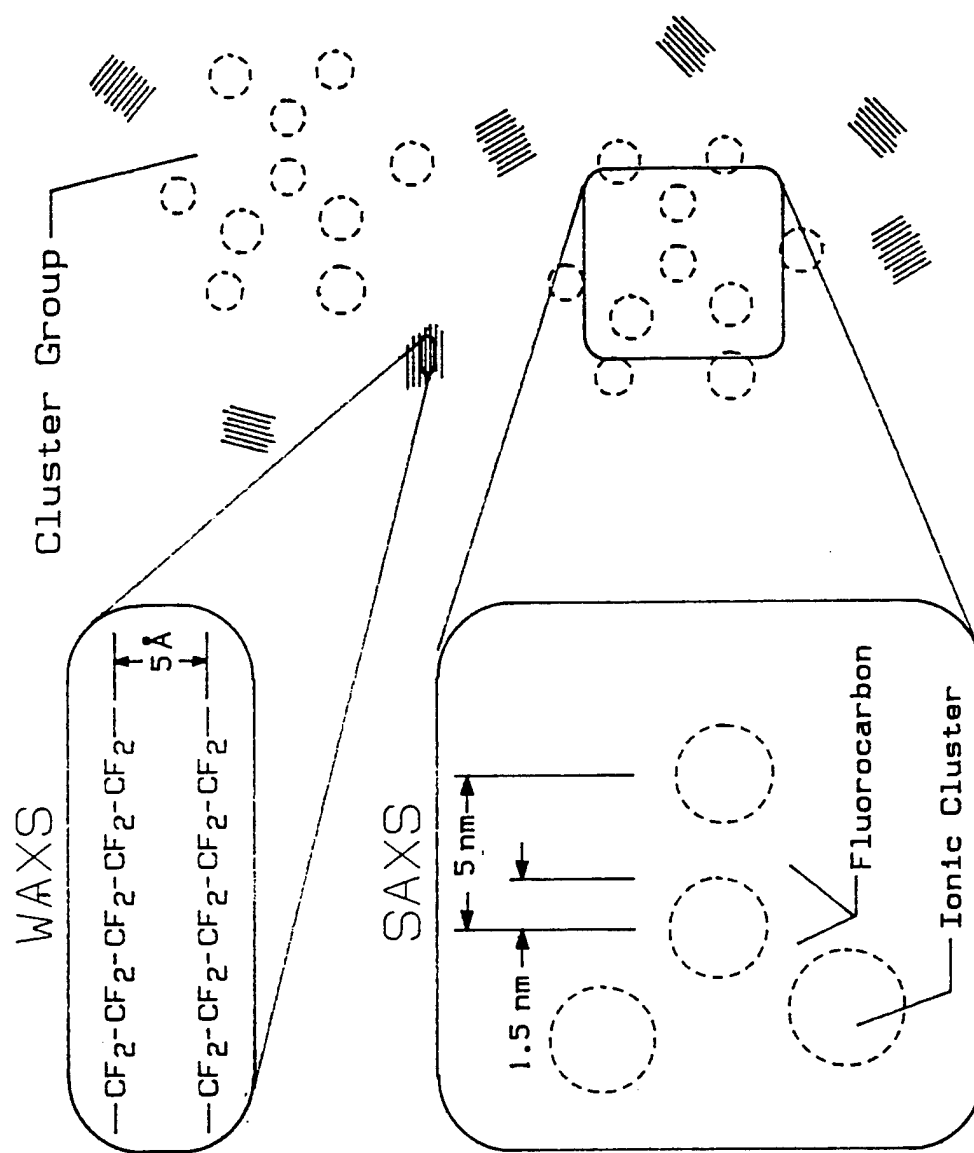
Key Point

STRENGTH VS CONDUCTIVITY

% xtal   # of Ionic Groups

Resist Swelling   Type of Group
                                          SO_3H vs - CO_2H

Physical   Hydration/Ionic Group

                                          Connectivity

METHANOL X-OVER POTENTIAL SOLUTIONS

Physical Reinforcement

- e.g., Gore Select

Change Crystallinity vs ionic Content

- New Monomers/Polymers

Chemical Crosslink

- New Monomers/Polymers

Low Hydration Conductive Groups

- New Monomers/Polymers

All of the Above

CLEMSON PROGRAM

New Polymers

- New Functional Groups
    - bis + poly perfluorosulfonimide
    - bis- perfluoro sulfones

- Thermoset Perfluoro Carbons

$$- CF_2DF = DF_2 \xrightarrow{\Delta}$$
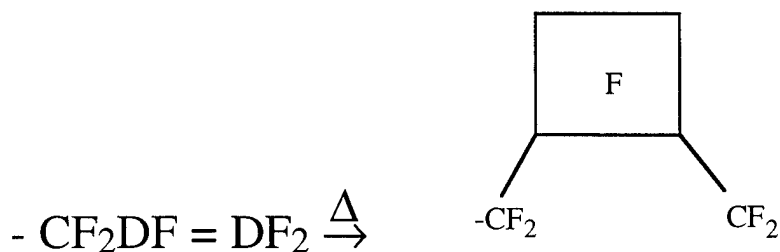
Polymer Catalyst Interface

Thin Film Technology

New Functional Groups

Electrode Kinetics

A PLASTIC Li/AIR BATTERY

K.M. Abraham
EIC Laboratories, Inc.
111 Downey Street
Norwood, Massachusetts 02062

A novel Li/O_2 battery unlike any metal/oxygen power sources developed to-date is described. This nonaqueous battery consists of a Li metal foil anode, a solid polymer electrolyte (SPE) membrane that conducts Li ions and a carbon composite electrode sheet made up of high surface-area carbon on which oxygen, the electroactive cathode material, accessed from the environment, is reduced during battery discharge to generate electric power. The organic polymer electrolyte membrane serves both as the separator that electronically insulates the cathode from the anode and the medium through which Li ions are transported from the Li anode to the oxygen cathode during discharge. The design of this novel battery is a radical department from that of traditional polymer electrolyte-based Li batteries in which the cathode comprises Li intercalating solid-state materials such as TiS_2, V_6O_{13}, $LiMn_2O_4$, and $LiCoO_2$.

The theoretical specific energies of some selected metal/O_2 chemical couples given in Table 1 illustrate the very high energy density available from a Li/O_2 electrochemical cell. The polymer battery described here is a novel and convenient way to harness this energy. A schematic of the cell is given in Figure 1. The SPE can be one of the many that we (1) or others (2,3) have developed. Table 2 lists the compositions and conductivities of potential electrolytes for the room temperature operation of the battery. Preliminary discharge data for cells fabricated with polyacrylonitrile-based electrodes are shown in Figures 2-4. A reaction process involving the adsorption of O_2 onto the carbon electrode, and its reduction according to reaction (1) and/or (2) can explain the observed results.

$$2Li + O_2 \rightarrow Li_2O_2; \qquad E = 3.10 \text{ V} \tag{1}$$

$$4Li + O_2 \rightarrow 2Li_2O_2; \qquad E° = 2.91 \text{ V} \tag{2}$$
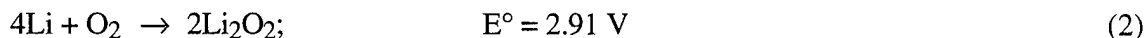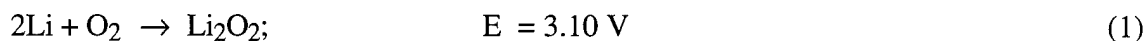
Standard cell potentials, $E°$, equations (1) and (2), were calculated using the standard Gibbs free energy of formation ($\Delta G°$) of -134 Kcal/mole for Li_2O and -145 Kcal/mole for Li_2O_2. A reaction between Li and H_2O could be ruled out as the source of the cell potential since $E°$ for the reaction, $Li + H_2O \rightarrow LiOH + 1/2H_2$ is only 2.08 V.

References

1. K.M. Abraham and M. Alamgir, *Solid State Ionics* **70/71**, 20 (1994).

2. M. Alamgir and K.M. Abraham, in *Lithium Batteries, New Materials, Developments and Perspectives*, Vol. 5, Chap. 3, Industrial Chemistry Library, G. Pistoia, Editor, Elsevier, New York (1993).

3. R. Koksbang, I.I. Olsen, P.E. Tonder, N. Knudsen, J.S. Lundsgaard, and S. Yde-Anderson, *J. Power Sources*, **32**, 175 (1990).

Table 1. Metal/Oxygen Couples

Chemical Couple	Standard EMF, $E°$	Specific Energy (Wh/Kg)	
		Including O_2	Excluding O_2
$4Li + O_2 \rightarrow 2LiO$	2.91	5200	11100
$4Na + O_2 \rightarrow 2Na_2O$	1.94	1675	2260
$2Mg + O_2 \rightarrow MgO$	2.93	3890	6460
$2Ca + O_2 \rightarrow CaO$	3.12	2990	4180
$2Zn + O_2 \rightarrow ZnO$	1.65	1090	1350
$4Al + 3O_2 \rightarrow Al_2O_3$	2.73	2930	8130

Table 2. Conductivities of Some Plasticized Polymer Electrolytes[2]

Electrolytes	Conductivity at 20°C S/cm
1. 21* PAN-38 EC/33 PC-8 LiAsF$_6$	2.1×10^{-3}
2. 37 PVdF-30 EC/30 PC-3 LiN(CF$_3$SO$_2$)$_2$	1.5×10^{-3}
3. 27 PVP-24 EC/21 PC/10 Triglyme-18 LiClO$_4$	1.1×10^{-3}
4. 37 PVS-30 PC/30 SL-3 LiAsF$_6$	1.5×10^{-4}
5. 24 PAN-38 EC/33 PC-5 LiPF$_6$	1.7×10^{-3}
6. 21 PAN-40 EC/36 PC-3 LiN(CF$_3$SO$_2$)$_2$	1.5×10^{-3}

[2]Ref: K.M. Abraham and M. Alamgir, *J. Power Sources* **43-44,** 195 (1993).
         M. Almgir and K.M. Abraham, "Room Temperture Polymer Electrolytes", Chapter 3 in Lithium Batteries, G. Pistoia, Ed., Elsevier, Amsterdam (1994).
         Solid State Ionics **70/71,** 20 (1994).

* Mole-percent

Section A-A

Cell

oxygen permeable membrane

composite carbon electrode on Ni current collector (+)

solid polymer electrolyte

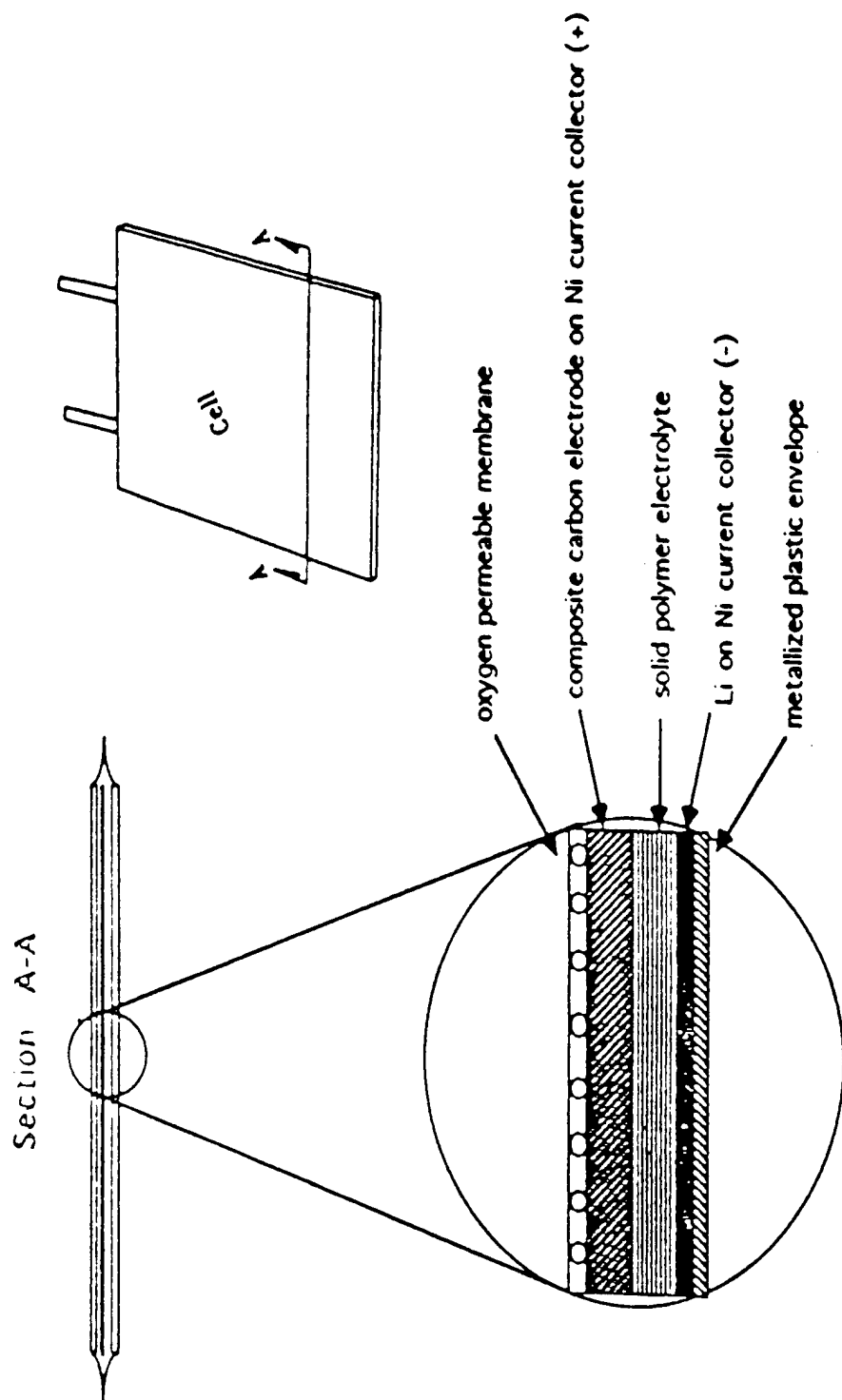Li on Ni current collector (-)

metallized plastic envelope

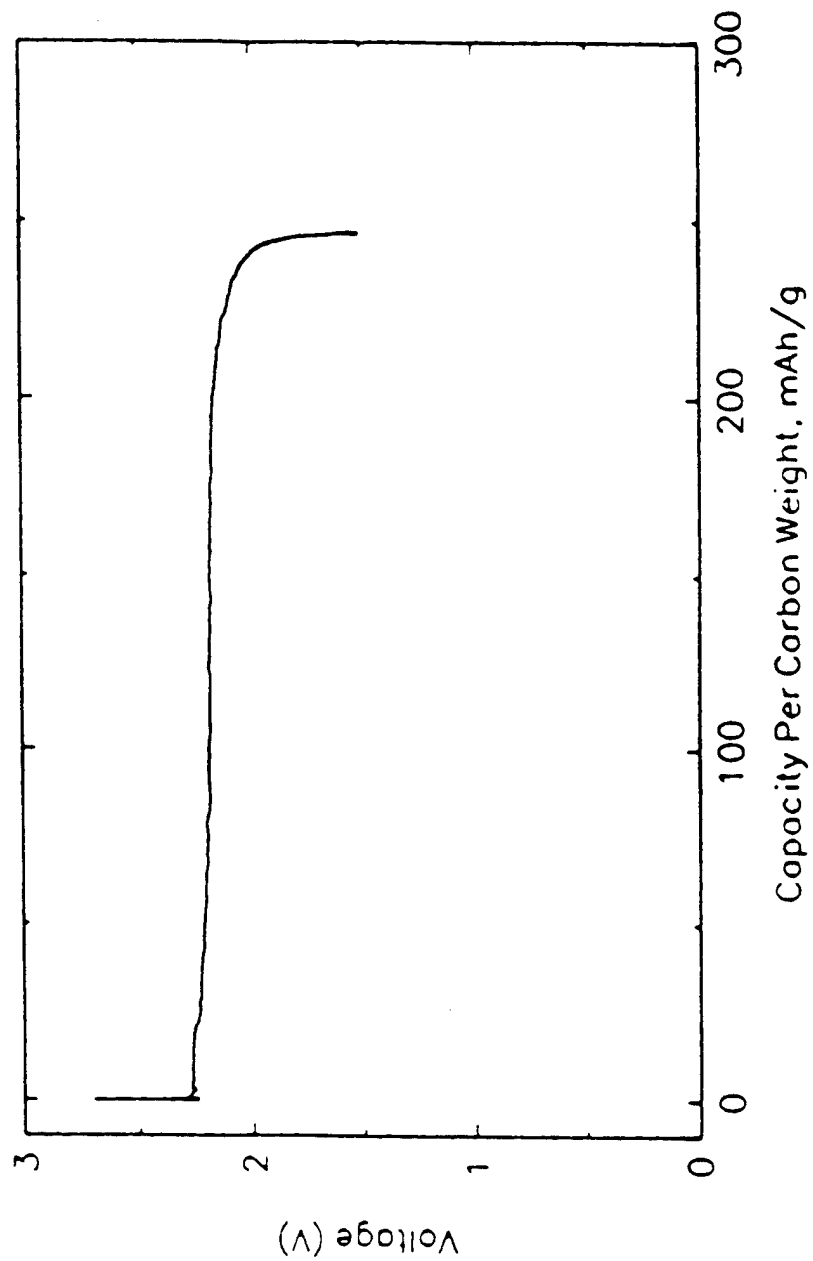Figure 1. Li/O₂ Polymer Battery.

3

Figure 2. Discharge of the plastic battery in oxygen atmosphere. The composite electrode is graphite. Current density = 0.1 mA/cm^2
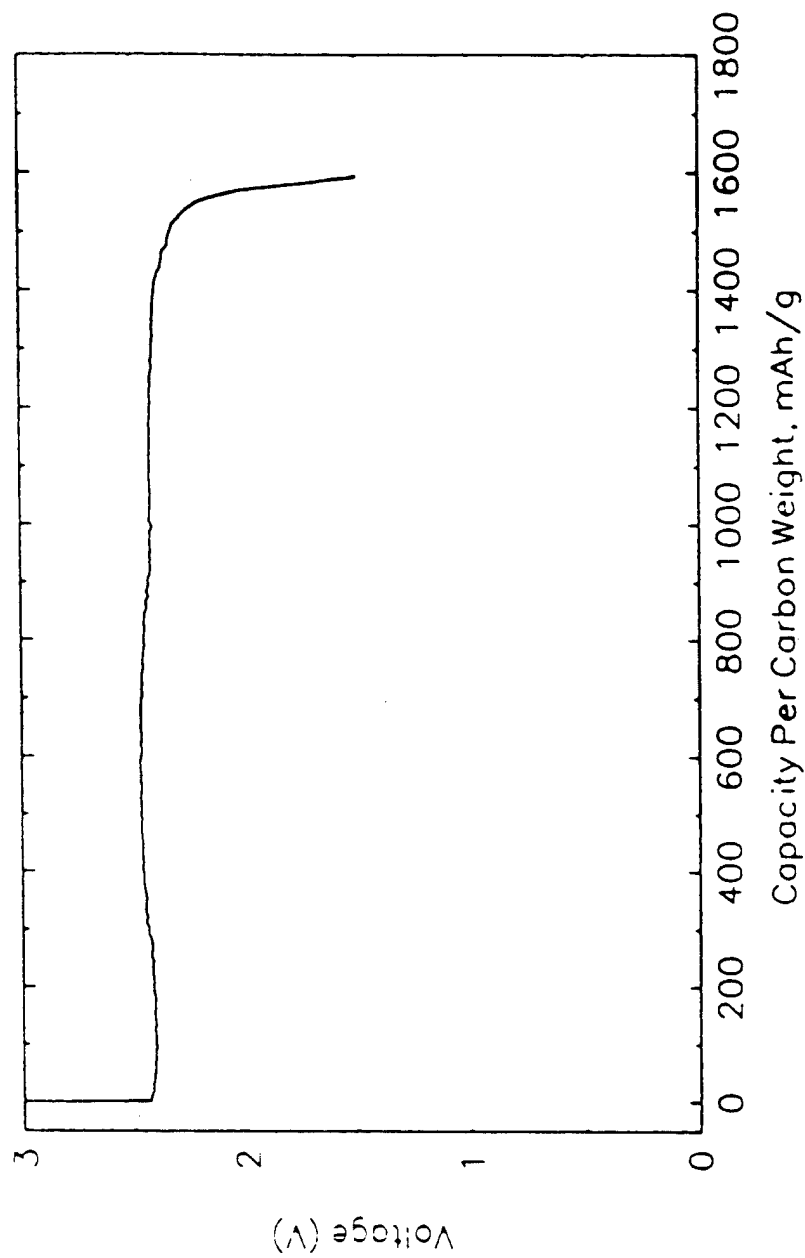
4

Figure 3. Discharge of Li/O₂ plastic battery in oxygen atmosphere. The composite electrode is carbon black. Current density = 0.1 mA/cm².
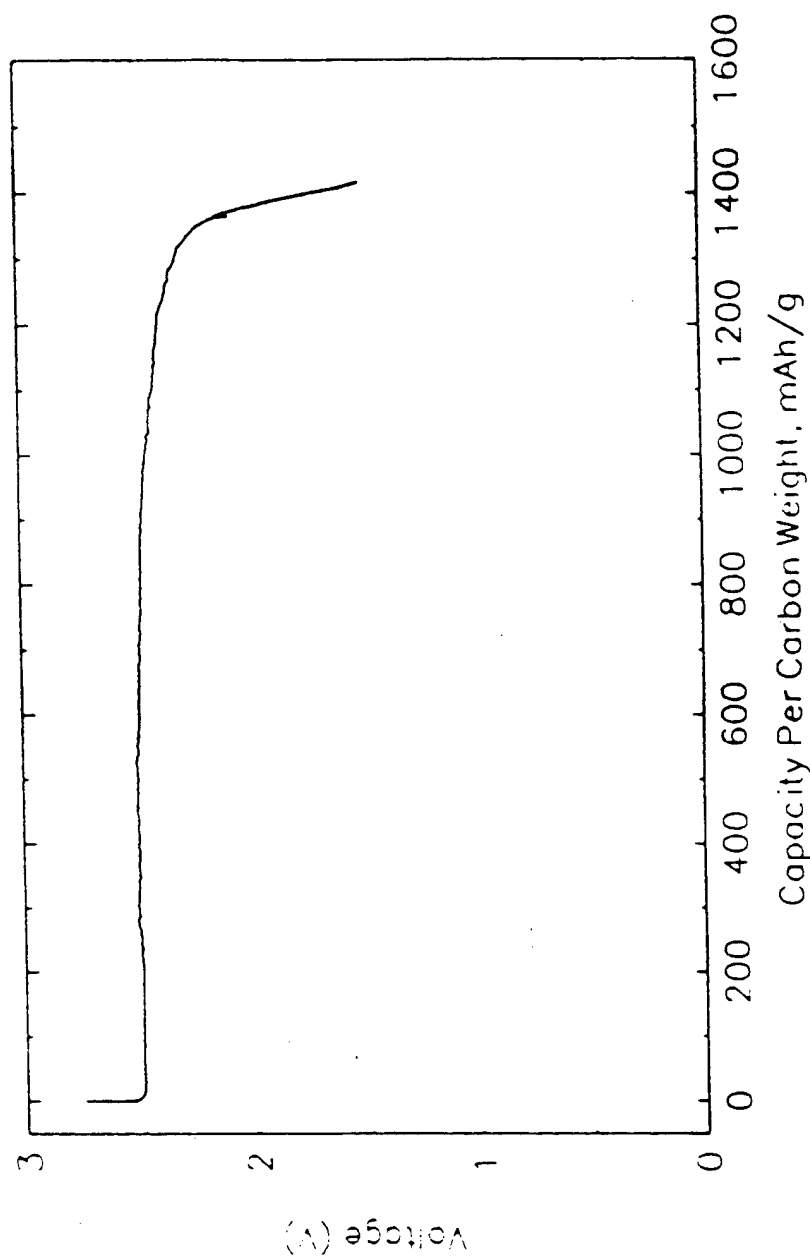
Figure 4. Discharge of the plastic battery in air. The composite electrode is carbon black. Current density = 0.1 mA/cm².

ZINC-AIR BATTERY TECHNOLOGIES

Ron Putt
803 Saddle Hill
Marietta, GA 30068

The zinc-air battery is characterized by very high specific energy and moderate specific power. When discharged over a period of weeks the specific energy can exceed 500 Wh/kg (ARL test results), and 400 Wh/kg has been demonstrated at the hundred-hour rate. The specific energy advantage for zinc-air degrades substantially for rates higher than C/10. Being an open system, zinc-air is vulnerable to dryout and carbonation, and should therefore be used in continuous duty applications unless a closure means is provided.

The first industrial use of zinc-air was to power remote signal devices, predominantly aids to navigation and railroad crossings. Both of these markets have seen rapid decline owing to the conversion of buoy power to solar photovoltaic/lead-acid (over 90%) and rural electrification. In the late 1970s Gould commercialized zinc-air button cells for hearing aids, and today's market share for zinc-air button cells exceeds 75% in this market.

Zinc-air makes an excellent primary battery, but efforts to make it rechargeable have been frustrated by the shape change phenomena of the zinc electrode and the dryout effect of the oxygen electrode during recharge. Recent progress by LBL, for example, in improving zinc electrode cycle life is not applicable to zinc-air, because the electrolyte formulations used impair oxygen electrode performance. And the only viable means of overcoming dryout is electrolyte management, via electrolyte circulation or direct water addition to the cells. This may be practical for stationary or vehicle batteries, but not for portable batteries. One may temporarily overcome the dryout problem by providing excess electrolyte, at a degradation of specific energy and energy density.

The keys to the high specific energy and energy density for zinc-air are the highly efficient and compact zinc electrode and the use of atmospheric oxygen. A typical zinc electrode comprises 60-70 weight per cent of zinc powder in a gelled potassium hydroxide electrolyte. Zinc utilization is typically over 90% at current densities below 10 mA/cm^2 and remains above 70% at current densities of 40 mA/cm^2. The zinc oxide discharge product remains in the electrode as a relatively compact phase. Anode weight and volume grow about 25% when the cell is fully discharged. Volume expansion can be accommodated by a collapsible foam beneath the anode, and pressure buildup can be avoided by venting the foam pore gases to the atmosphere (MATSI patent).

The zinc electrode must be protected from direct oxidation during the last half of discharge if high utilizations are to be achieved. For a fresh cell the zinc is well protected from cathode oxygen because the cell is flooded with electrolyte and oxygen solubility is very low. However, after about 50% discharge the zinc electrode becomes dryer (less free moisture) because of the chemical and physical binding of water to the high surface area zinc oxide discharge product. Thus, in turn, pulls moisture from the separator and oxygen electrode, opening up paths for gaseous oxygen to the remaining zinc metal. It is, therefore, desirable to use a gas-impermeable membrane to block oxygen transport. The membrane can be used in combination with a non-woven separator made of, for example, PVA.

The oxygen electrode must have a peroxide decomposition catalyst to achieve efficient cell performance. Not only does the catalyst raise the oxygen electrode voltage, but it also minimizes the transport of perhydroxide to the zinc electrode. Anode utilizations in cells without a peroxide decomposition catalyst can be 20-30% lower than those of cells having a catalyst. Manganese oxides, such as manganese dioxide, are an excellent choice. Cobalt oxides and precious metals are

to be avoided because they solubilize and diffuse to the zinc electrode, causing excessive hydrogen gassing.

The next application of zinc-air technology will likely be for fleet propulsion Electric Fuel Limited (Jerusalem) has a program with Deutsche Post to deliver and service a fleet of 64 vehicles, a combination of pickups and vans, which have mechanically-refuelable zinc-air batteries. The program includes the construction and operation of a 10 kg per hour zinc fuel reprocessing facility in Bemen.

SOLDIER SYSTEM BATTERY PACK

Chemistry: primary zinc-air

Electrical Specifications:

100 W, 12 V, 1000 Wh

Electrodes:

Anode:

- 65 w% zinc powder in 35% KOH gelled electrolyte.

Cathode:

- 8 mil gas diffusion electrode

Separator:
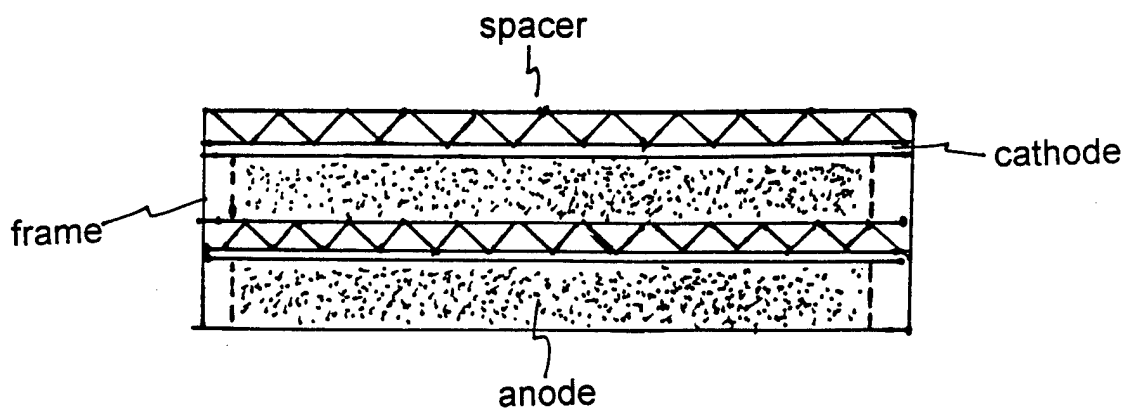
- PVA non-woven + membrane

Design Basis:

Current Density: 8.3 A / 180 cm^2 = 46 mA/cm^2

Anode: ~ 3 g/cm^3; 65% utilization; 4.2 mm thick

Voltage: 1.1 V average/cell; 1.0 V minimum/cell

Stack: 12 bipolar cells

CELL CUTAWAY
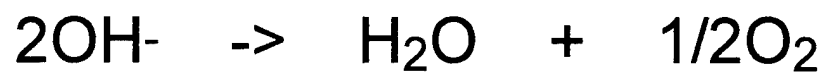
THE PROBLEM WITH RECHARGE:

DRYOUT

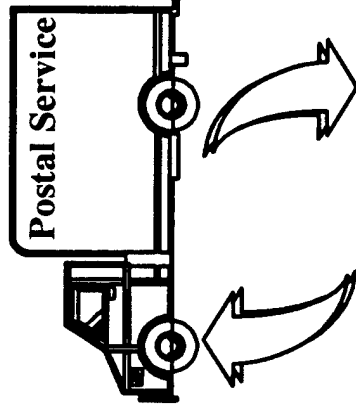(1) $\text{deltaV}|_{chg} \sim 800 \text{ mV}$

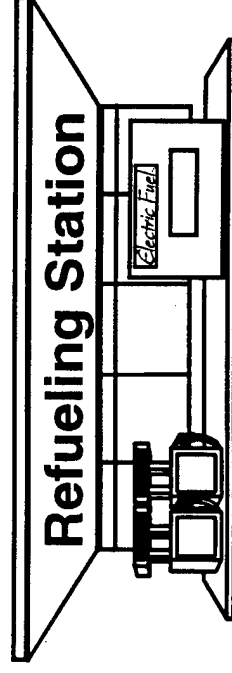$$2OH^- \quad \rightarrow \quad H_2O \quad + \quad 1/2O_2$$

$$(2) \qquad\qquad (3)$$

The Solution: Electrolyte Management

A System Solution

☐ A zinc-air Battery

☐ A Refueling system

☐ A Regeneration system

Postal Service

Refueling Station
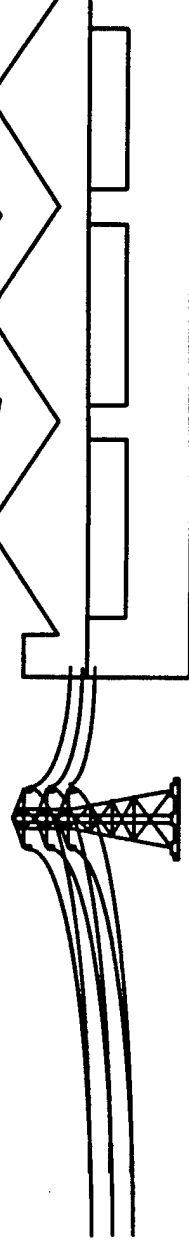
Electric Fuel

European Programs

- Deutsche Post AG (German Postal Service)
  - Fleet of 50,000 vehicles
  - Intent to convert 25,000 to EVs
  - Selected the Electric Fuel System only
  - TÜV laboratory and in-vehicle testing
- Deutsche Telekom (German Telecom)
  - Fleet of 40,000 vehicles
  - Intent to convert 15,000 to EVs
- Other Programs in Italy, Germany, the US, etc.

Electric Fuel™

The Deutsche Post Field Test (95-97)

- [ ] 64 Mercedes-Benz vans and GM Opel pick-ups

- [ ] Largest advanced-battery fleet test ever

- [ ] Most energy ever put into EV's - equivalent to tank of gasoline/diesel

- [ ] Sponsored by EV-committed customers: Deutsche Post, Telekom, Municipalities and Utilities

- [ ] Participation of leading industrial companies: Mercedes-Benz, GM-Opel, Siemens, Hoechst

Electric Fuel™

Cost Considerations

- ❑ **Battery**
  - ❑ Lowest cost technology, under $70/kWh

- ❑ **Infrastructure**
  - ❑ Regeneration centers
  - ❑ Refueling systems
  - ❑ Total cost $10 to $20 per kWh battery

Electric Fuel™

Life-Cycle Cost - Cargo Vehicle

(first 120,000 km)

	Electric Fuel Zinc-Air	USABC Mid-term
Range, km	300	125
Payload capacity, kg	1,181	988
Battery cost , per kWh	$75	$150
Total battery cost (pro-rated)	$9,300	$15,600
Battery cost per km	6.6 cents	13.2 cents
Refueling/Recharging		
Electricity	3.0	3.0
Infrastructure - direct	8.6	4.1
Recharging cost per km	11.6 cents	7.1 cents
Total cost per km	18.2 cents	20.3 cents

Electric Fuel

Life-Cycle Cost - Passenger vehicle

(first 120,000 km)

	Electric Fuel Zinc-Air	USABC Mid-term
Range, km	300	125
Cycle life	400	600
Battery cost , per kWh	$75	$150
Total battery cost (pro-rated)	$4,440	$8,040
Battery cost per km	3.7 cents	6.7 cents
Refueling/Recharging		
Electricity	1.4	2.2
Infrastructure - direct	4.0	0.8
Recharging cost per km	5.4 cents	3.0 cents
Total cost per km	9.1 cents	9.7 cents

Electric Fuel

Summary

☐ A "format" similar to industry standards — for users and suppliers

☐ Independent verification by leading testing institutes in Europe

☐ Partnerships with world-class institutions

☐ A cost-effective, energy-efficient, EV solution

Electric Fuel

FUEL CELL ATTENDEE LIST

Dr. Sol Gilman
U.S. Army Research Lab-EPSD
ATTN: AMSRI-EP-PB
2700 Pearl Harbor Way
Ft. Monmouth,   NJ   07703-5601

Prof. Robert F. Savinell
Department of Chemical Engineering
Case Western Reserve University
Cleveland, OH 44106

Dr. Günther G. Scherer
Paul Sherrer Institute
Würenlingen and Villigen
CH-5232 Villigen PSI
Switzerland

Dr. Oliver J. Murphy
Lynntech, Inc
7610 Eastmark Drive #105
College Station, TX 77840-4024

Dr. Shimshon Gottesfeld
Los Alamos National Laboratory
MEE11-Electronics Research Group
PO Box 1663
MS D 429
Los Alamos, NM 87545

Dr. Anthony B. Laconti
Giner, Inc.
14 Spring Street
Waltham, MA 02254-9147

Dr. Charles Martin
Department of Chemistry
Clemson University
Box 341905
Clemson, SC 29634-1905

Dr. Patrick Grimes
Pat Grimes Associates
504 Mountain Avenue
Westfield, NJ 07090-3036

Dr. K.M. Abraham
EIC Laboratories, Inc.
111 Downey Street
Norwood, MA 02062

Mr. Ronald Putt
803 Saddle Hill
Marietta, GA 30068

Mr. Harold Christopher
U.S. Army CECOM
Attn: AMSEL-RE-AS-BE
Ft. Monmouth, NJ 07703

Dr. Robert J. Nowak
Office of Naval Research
ONR 331
800 N. Quincy Street
Arlington, VA 22217-5660

Dr. Lawrence H. Dubois
Defense Sciences Office
Advanced Research Projects Agency
Room 743
3701 N. Fairfax
Arlington, VA 22203-1714

Mr. James K. Stedman
Institute for Defense Analyses
10 Harvest Lane
Glastonbury, CT 06033

Dr. Richard Paur
US Army Res Office
AMXRO-CB   PO Box 12211
Research Triangle Park, NC 27709

Dr. Peter Fedkiw
US Army Res Office
AMXRO-CB   PO
Box 12211
Research Triangle Park, NC 27709

Dr. Donald Maricle
International Fuel Cells
195 Governor's Highway
PO 739
South Windsor, CT 06074